MODERN SYNTHETIC RUBBERS

By the Same Author

MODERN RUBBER CHEMISTRY (*Hutchinson*)
MODERN PLASTICS (*Chapman & Hall*)

HARRY BARRON
PH.D., B.SC., F.R.I.C., F.I.R.I., F.P.I.

MODERN SYNTHETIC RUBBERS

THIRD EDITION
REVISED AND ENLARGED

LONDON
CHAPMAN & HALL LTD
37 ESSEX STREET W.C.2
1949

FIRST PUBLISHED, 1942
SECOND EDITION, 1943
REPRINTED, 1945
THIRD EDITION, 1949

CATALOGUE No. 16/4

PRINTED IN GREAT BRITAIN BY BUTLER & TANNER LIMITED, FROME AND LONDON

BOUND BY G. & J. KITCAT LTD., LONDON. FLEXIBACK BINDING

To

GRACE, ANTHONY, HELEN
RICHARD AND PENELOPE

PREFACE TO THIRD EDITION

AFTER atomic fission I consider that the large-scale production of synthetic rubber ranks as the outstanding technical achievement of the war period. The speed and scope of the U.S. production are without parallel in the history of chemical manufacture.

Now that the iron curtain of wartime secrecy has been lifted, we can gain a fuller appreciation of the tremendous advances that have been made.

All the German synthetic rubber secrets have now been uncovered. Combined Service Intelligence Reports on German industry constitute a veritable mine of information on the subject. There are some who underestimate the value of these Reports. I disagree entirely with this attitude. After all, the basic principles of synthetic rubber production are generally known. Those who sought entirely new fundamental principles were doomed to disappointment. It is the mass of details and " know-how " which is of outstanding value.

The publication of these Reports so rapidly may appear to show up developments in other countries in an unfavourable light. This is illusory. Many apparently novel German developments were anticipated in other countries. Patent specifications and information regarding these developments were withheld from publication during the war period. They are now only slowly being allowed to emerge from cold storage. Even so, there is far less information and detail given than is available in the Reports on German Industry. With the best will in the world no commercial concern nor any Government Department would disclose such detail except under duress.

It has been interesting to observe how apparently insuperable problems in the use of synthetic rubbers have gradually been solved. Even in this country manufacturers have become accustomed to using synthetic rubbers and no longer regard them with apprehension and horror. With the passing of time, control of the nature and behaviour of the synthetic rubbers has become more and more definite. The production of " tailor-made " types for special purposes is no longer so bombastic an idea as at one time seemed the case.

As foreshadowed, the influence of synthetic rubbers on plastic activities has been profound. With the return of natural rubber into circulation the slack in U.S. synthetic rubber production has been increasingly taken up by increases in plastic production often in the same plants. Rubber manufacturers accustomed to using synthetic

rubbers have become equally accustomed to handling plastics. One of the most significant trends is the use of synthetic rubbers together with plastics. Perhaps the most notable examples are the use of butadiene-acrylonitrile rubbers together with polyvinyl chloride, and the growing use of thermosetting resins as vulcanizing agents.

As anticipated too, the availability of synthetic rubbers has had a profound influence in keeping down the price of natural rubber.

In spite of the tremendous strides in the use of petroleum derivatives it is fascinating to observe how synthetic rubbers are still dependent on coal as the basic raw material. The advances in the use of agricultural products have been temporarily halted owing to world food shortages.

In Great Britain there appears to be no interest in the production of synthetic rubbers, but what a profound influence they have had on natural rubber research work! The potential competitive pressure of synthetic rubber has undoubtedly accelerated this work and very important developments can be anticipated.

In this edition I have included a section on compounding. This is a very confusing aspect of the manufacture of products from rubber or synthetic rubbers. I hope the chapter may be of some service in presenting a reasonably clear picture of this aspect.

I have included a number of tables in Chapter 7 which show how costs for large-scale production of synthetic rubbers have been derived. Some of these tables may be out of date. They are included because they have very high educational value. The average technical man is very often quite unconscious of how the costs of materials are evaluated on the large scale. It is important that he should become aware of some of these important aspects of his existence.

The U.S. Rubber Act of 1948 has stabilized the position of synthetic rubbers. Facilities are to be maintained to produce 665,000 tons of synthetic rubbers annually. The use of 225,000 tons per year becomes mandatory. The development of low-temperature rubbers marks a great step forward. It reduces still further the technical superiority of natural rubber.

Finally, the political unrest in Malaya and Indonesia prevailing at present obviously strengthens the position of synthetic rubbers.

HARRY BARRON.

SOUTHAMPTON,
1948.

PREFACE TO SECOND EDITION

At the best of times a subject such as synthetic rubber would be difficult to handle. In these days events move so rapidly under the pressure of war conditions that by the time the first edition had been published it was already out-of-date. A flood of developments in the United States made it quite clear that another revised version would rapidly be required.

The book was written when the seriousness of the rubber situation had just made itself felt in the United States. An assortment of U.S. Senate Committees were examining different aspects of the problem. The earlier synthetic programmes had been impressive. When the true position became apparent, the programmes were stepped up until they became almost astronomical. The practical difficulties introduced a number of commercial by-products. Animosities were aroused. Competitive interests clashed.

Investigation of the patent position in the synthetic rubber field disclosed an unsatisfactory situation, hampering the war effort. This automatically led to the policy whereby patents in the synthetic rubber field were made generally available. One consequence of the disclosures made in this connection was to make the United States public fully conscious of the situation. It became clear that more intensive co-ordination was necessary. President Roosevelt appointed the Baruch Committee to sort the position out. Its recommendations were made public just as *Modern Synthetic Rubbers* was published. It laid down a programme which is now being pushed through with the greatest determination.

In the early days rubber from oil had all the limelight, and the major part of the programme was based on oil products. Another Senate Committee (the Gillette Committee) has since shown clearly that agriculture is perhaps an even better source of raw materials.

The difficulties of handling the new materials have been tackled with commendable American thoroughness. Moreover, what is perhaps even more laudable, the results have been published. New compounding ingredients have had to be developed. United States industry is all set to take the new materials in any quantities. There is the general determination to bring these materials on to a permanent basis.

And what of this country? We stand where we did—wondering

what may be retrieved from the Japs, and when! There are as yet few signs of activity in the synthetic rubber field.

Most people agreed with my strictures about our lack of research and development. Some disagreed violently. I stick to my opinion. Developments in plastics and associated chemical activities are keyed to a large synthetic rubber industry. We shall in due course regret our backwardness and reluctance to take the plunge.

It is heartening, however, to see the realization in all quarters that we must encourage development as far as possible. It is to be hoped that these will not remain as pious hopes, but will be put into practice.

Having stated that I regarded the book as something to bite upon, I could hardly expect to get away unscathed. Nor did I. It was well and truly "bitten" at—in most cases justifiably and constructively. Other critics just bit.

The first edition contained many errors. I am deeply grateful to those people who were kind enough to inform me of them. In particular I would express my gratitude to Mr. G. H. Wyatt, Ph.D., F.I.C., who has gone to a great deal of trouble in this respect. These errors have been rectified.

I wish to thank all those who have made constructive criticisms of various aspects. For example, Mr. W. H. Stevens, of the Monsanto Chemical Company, Ltd., has very kindly "vetted" my chapter on Thioplasts.

HARRY BARRON.

SOUTHAMPTON,
1943.

PREFACE TO FIRST EDITION

The subject of synthetic rubbers is of the greatest National importance. It is a topic of everyday conversation, although very little is known about them, even in technical circles. It is regrettable that a great deal of nonsense has been published on the subject. Unfortunately there is no recent work of reference concerning synthetic rubbers.

Oddly enough, neither the Germans nor the Americans have so far published any books on the subject. Information is scattered far and wide among the technical journals, the scientific magazines, and various commercial leaflets and brochures. I have endeavoured to bring together as much of the information available in as palatable a form as possible. The most comprehensive mass of information on synthetic rubber is published in the U.S.S.R., and I have only had access to those few articles which have been translated.

I have thoroughly enjoyed this very formidable task, for I have long been one of the most ardent advocates for a synthetic rubber industry to be established in this country. I foresaw its normal commercial expansion, and have wondered why we did nothing about it here. As long ago as October 27th, 1936, I wrote in the *Evening Standard*: " as a form of long-term insurance it would be well worth the while of the Government to take an interest in the production of synthetic rubber ". As events have turned out this was almost prophetic. A few weeks later, on November 23rd, in the same newspaper, I wrote: " Vinyl resins obtained from acetylene will in the near future attain an industrial importance which at present it is not possible to estimate ". But until recently all my endeavours to stir up active interest have fallen on deaf, not to say hostile, ears. It is very grievous that at the present time when the natural rubber position is so unhappy, Great Britain should be left high and dry without any synthetic rubber industry, and without one in sight.

If only the powers-that-be could understand what they are doing in holding up the development of such an industry! But I despair of making them appreciate the full significance, of making them conscious of the many considerations other than that of synthetic versus natural rubber. Let me have yet another try.

On all sides one hears the opinion expressed very glibly that we are entering upon a Plastics Age. I believe this to be the case, but what does it mean? If it means anything at all, it is that plastics will play a very great part in our life. But this does not mean an

existence dominated by the moulded articles with which we are so familiar. Not at all. It means that plastics will play a very important part in building aircraft, motor-cars, ships, houses, and structures generally. It means that they will have a great influence on many industries, such as the electrical industries, the engineering industries, and so on. Our livelihood, our comfort, and our happiness may be utterly bound up in their use. Already the design of many machines of war are deeply affected by the application of both synthetic rubber and plastics.

Where do synthetic rubbers come into this picture? Well, they have their own physical part to play: a very important part. Of that there can be no doubt. But the important thing is that in many cases precisely those plastics which will be of such pre-eminent importance are also involved in the production of synthetic rubber, either directly or as by-products. That single fact enables them to be produced on a very large scale and very cheaply, since all the major costs are borne by the synthetic rubber production. In other words, synthetic rubber paves the way for the Plastics Age. Together with the synthetic rubber industry you will have a healthy expanding plastics industry; without it, the thermoplastic industry will inevitably be a hothouse plant constantly requiring artificial stimulation. And those many dependent industrial activities will be correspondingly affected —adversely.

In Great Britain, the exigencies of war have brought home the fact that in many directions we are considerably behind in technical progress. We have certainly been travelling on the train of progress, but with our backs to the engine—and third class! There has been no money available for development. We can only see the receding landscape. Our technical men have not been encouraged to see the new horizons and opportunities that are continually being opened up. Our national inherent creative ability has been allowed to go to waste. Certainly a great part of it should be directed into the field of synthetic rubbers and the associated materials which will be the basis of the Plastics Age.

Advocacy of synthetic rubber in Great Britain has always been extremely unpopular. So much so, that on one occasion when I had the temerity to suggest such a thing, I was nearly thrown out of a meeting of the Institution of the Rubber Industry, early in 1939—an unprecedented occurrence. Oddly enough, that particular meeting was a Sales meeting for Buna rubbers!

But during the last year or two, the murmurings of synthetic rubber activity from abroad have begun to have some effect. The

worried rumblings of the uneasy American tyre manufacturers were very evident. The precautionary activity in the United States clearly showed the trend of things to those realistic people who realized the implications of bringing rubber so many thousands of miles under war conditions. It only needed the attack of the Japanese at Pearl Harbour to let loose the greatest torrent of scientific and technical development on synthetic rubbers that the world has yet seen. This work is going to have a most profound effect on world progress in the near future. It will certainly accelerate the arrival of the Plastics Age.

Early in 1941, a year before the need became so definite as to dispose of all doubts about the future of synthetic rubber, with commendable vision, the Editor of *The Rubber Age* agreed to my suggestion that he should publish a series of articles on synthetic rubbers. This series still continues. I have drawn freely on these articles in writing this book, and I must thank Mr. Pickett, Mr. Hunter, and Miss Fenn for their encouragement and enthusiasm.

The implications of synthetic rubber production on plastics development have always been quite clear to me, and I was able to persuade Mr. Wilkins of *British Plastics* to allow me to write a series of articles dealing with this aspect. I have to thank him for permitting me to draw freely on these articles.

The question of terminology has been a very thorny one. I expect to be assailed for indulging in a certain degree of dualism. But so far as nomenclature is concerned, I do not believe it is possible at any given moment to switch over from one set of terms to another. The only way is to change over gradually, which I have endeavoured to do.

I apologize in advance for any errors and omissions, but the work has been written under certain difficulties. For one thing, it has been a spare-time occupation. My days have been, and are, fully occupied in development work and large-scale manufacture of products involving many of the materials described in this book. The evenings and nights of these times, and in these parts, are not always conducive to constructive and creative work. All too often the pen has to be laid aside at the behest of the more urgent and insistent call of the air-raid siren.

Be that as it may, I present this book in the hope that it may be regarded as a contribution to knowledge in this sphere of activity. It will at least provide something to bite on, some basis on which, no doubt, many better books will be written.

HARRY BARRON.

SOUTHAMPTON,
1942.

CONTENTS

PART I

GENERAL CONSIDERATIONS

PART II

CHEMICAL AND PHYSICAL BACKGROUND OF SYNTHETIC ELASTIC MATERIALS

PART III

TECHNOLOGY OF SYNTHETIC ELASTIC MATERIALS

PART I

GENERAL CONSIDERATIONS

CHAPTER I

NATURAL RUBBER AND SYNTHETIC RUBBER-LIKE MATERIALS

THERE are at the present time a large number of materials referred to as synthetic rubbers. They include many which have only lately come to be classed in this category. Table 1 lists many of these products. In one sense this represents only a summary, for each type divides up into variations on the main theme. It is evident, therefore, that the study of synthetic rubber is already a formidable task. And the really intensive universal interest has only recently started.

Efforts to produce synthetic rubbers have passed through a number of distinct phases. The first and longest phase was the academic one, in which chemists endeavoured to break down natural rubber in order to determine its composition and structure, while at the same time endeavouring to utilize the breakdown products to rebuild the original material. They were able to obtain a number of interesting materials, but these were mere laboratory curiosities.

The second phase during the early part of the century coincided with the period during which the rubber plantations in the Far East were beginning to make some progress. It was marked by two outstanding technical developments. One was the discovery of useful starting materials in the form of coal and limestone, while the other was a better realization of and improvement in the process of polymerization. The climax of this phase came during the last war, during the final stages of which Germany was actually manufacturing with considerable difficulty some 300 tons per month of methyl rubber. The end of that war also saw the finish of this production. Thereafter there was complete stagnation until 1925, when the price level of raw rubber reached such a ridiculous height that the greatest possible stimulus was given for the production of synthetic material. This marks the third phase during which large-scale research in several countries yielded an increasing number of new synthetic materials. These were gradually combed out, and the more promising ones brought to the stage of practical application and nearer to the goal of becoming commercial commodities. During this period extending up to 1933, the chief efforts were in the direction of finding suitable raw materials for large-scale production.

The fourth phase was the development of manufacturing establish-

Table 1. Synthetic Elastic Materials

1. BUTADIENE POLYMERS	
Buna 85	*I.G. Farbenindustrie (Germany)*
Buna 115	*"* *"*
S.K.A.	*U.S.S.R.*
S.K.B.	*"*
2. BUTADIENE—STYRENE COPOLYMERS	
GR-S	*U.S. Government*
Buna S	*I.G. Farbenindustrie (Germany)*
Buna S-3	*"* *"*
Buton S	*"* *"*
Chemigum IV	*Goodyear Corp. (U.S.)*
Hycar OS (Types 10, 20, 30)	*Goodrich Corp. (U.S.)*
Nubun	*United States Rubber Co. (U.S.)*
Polysar	*Polymer Corp. (Canada)*
3. BUTADIENE—ACRYLONITRILE COPOLYMERS	
Buna N	*I.G. Farbenindustrie (Germany)*
Butaprene	*Firestone*
Chemigum I	*Goodyear Corp. (U.S.)*
Hycar OR (Types 15, 25)	*Goodrich Corp. (U.S.)*
Nubun	*United States Rubber Co.*
Thiokol RD	*Dow Chemicals Co. (U.S.)*
Perbunan	*Standard Oil Co. (U.S.)*
4. CHLOROPRENE COPOLYMERS	
GR-M	*U.S. Government*
Neoprene (Types CG, E, FR, G, GN, KN, M)	*Du Pont de Nemours (U.S.)*
Sovprene	*U.S.S.R.*
5. THIOPLASTS	
GR-P	*U.S. Government.*
Ethanite	*Belgium*
Novoplas	*Imperial Chemical Industries, Ltd. (Gt. Britain)*
Perduren	*I.G. Farbenindustrie (Germany)*
Thiokol (Types A, B, D, F, FA, M, N, ST)	*Dow Chemical Co. (U.S.)*
Vulcaplas	*Imperial Chemical Industries, Ltd. (Gt. Britain)*
6. ISOBUTYLENE POLYMERS	
Vistanex	*Standard Oil Co. (U.S.)*
Oppanol	*I.G. Farbenindustrie (Germany)*
7. ISOBUTYLENE-ISOPRENE COPOLYMERS	
GR-I	*U.S. Government*
Butyl Rubber (Types B—1·45, B—3)	*Standard Oil Co. (U.S.)*
8. POLYESTER RUBBERS	
Norepol	*U.S. Dept. of Agriculture*
Agripol	*Reichhold Chemicals (U.S.)*
Paraplex G-100	*"* *"*
Vulcaprene	*Imperial Chemical Industries, Ltd. (Gt. Britain)*
9. POLYVINYL COMPOUNDS	
Corvic	*Imperial Chemical Industries, Ltd. (Gt. Britain)*
Geon	*Goodrich Corp. (U.S.)*
Igelite	*I.G. Farbenindustrie (Germany)*
Vinylite	*Carbon & Carbide Corp. (U.S.)*
Saflex	*Monsanto Chemicals Corp. (U.S.)*
Gelva	*Shawinigan Corp. (U.S.)*
Chemaco	*Chemaco Corp. (U.S.)*
Tygon	*U.S. Stoneware Co. (U.S.)*

ments on an ever-growing scale in several countries, notably in the strongly nationalistic states where no hindrance was imposed and every encouragement given for large-scale production. This led up to a very considerable scale of manufacture with a somewhat questionable commercial prospect.

The fifth phase was one in which large-scale production of synthetic rubber had become a necessity, and natural rubber played a minor part. The amazingly successful realization of the plans for the production of an enormous quantity of synthetic rubber in the United States marked the end of this phase. The stage is now almost set for the competition between synthetic rubbers and natural rubber.

Since synthetic rubber is now openly intended for use in the place of rubber the behaviour must be considered in relation to the behaviour and properties of natural rubber. This is necessary to bring the subject into true perspective. Synthetic rubber must be weighed up against the industrial and technical background of natural rubber.

What relationship is there between synthetic rubber and raw rubber? What is their commercial significance likely to be? Is there any real permanent threat to the interest of the plantation industry, etc.? These are all questions which must be examined and answered.

The Part played by Rubber in Modern Life. Rubber is indispensable to modern civilization. Its importance in every form of transport for tyres and tubes is self-evident. But in its other applications it plays equally important rôles. It is a revelation to consider to what extent industry in general, indeed life in general, is dependent upon rubber. About 80 per cent. of all rubber is used in the motor industry, mainly for tyres. This applies to passenger transport, goods transport, and private cars. A large proportion of the remainder goes into what are known as mechanical goods, which include such articles as belting, packings, moulded goods, hose, and innumerable other types of products. Most of these articles are absolutely vital to the operation of the industry in general. Without them industries could come to a standstill.

TABLE 2. UNITED STATES RUBBER CONSUMPTION, 1939

	Per cent.
Tyres	63·6
Tubes	9·2
Other tyre uses	3·1
Mechanicals	9·0
Boots and shoes	6·8
Druggists, sundries and sports goods	5·0
Other uses	3·3

A large quantity of rubber is made into rubber footwear, into soles and heels, which all play an important part in the daily life and health of the community. Thousands of tons of rubber are used for covering wires and cables playing a vital part in communication and transmission. Lesser quantities of rubber find their way into such essential products as rubberized fabrics for rainproof and other sheetings, into numerous druggists' sundries, into rubber springs and mountings, into rubber thread, into sponge rubber, and many other vital types of products. In fact, rubber cushions the shocks of a turbulent world.

The Rubber Industry as a Service Industry. The rubber industry is chiefly a service industry. It produces indispensable parts required for the successful operation of nearly every other industry. The diversity is shown by the fact that one firm alone, B. F. Goodrich Co. in the United States makes more than 35,000 articles. Without rubber the various forms of transportation could not run, the communication system would break down, national health would be adversely affected, the shoe and clothing industry would suffer, etc. Rubber is of the greatest possible importance in tyres on tractors for agricultural use. The change-over from steel wheels to pneumatics has had a profound effect on agricultural development.

Importance in Warfare. This general statement applies to ordinary industrial obligations. Introducing military considerations merely emphasizes what has been stated. Present-day mechanized warfare implies rapid and smooth transport of armies and their supplies, which means that they must run on rubber. Modern mechanized warfare cannot be waged without rubber for transport.

But the fighting services rely on rubber for other activities than transport. Warfare is now a very scientific operation implying more instruments of control, more equipment, and more protective devices. In many of these aspects rubber has made profound contributions.

Vehicles such as lorries, cars, etc., must be equipped with tyres, or with rubber tracks, in many cases requiring to be bullet-proof and resistant to puncture. Tanks also must be equipped with various forms of rubber tracks, and other rubber articles. It has been stated that a 30-ton tank contains nearly a ton of rubber, while a modern battleship is said to use about 70 tons.

Another important development involving the use of rubber is in self-sealing petrol tanks and hose for aircraft. In war, as in peace, hosepipe of every description is of the greatest importance. Ordinarily hose is necessary for the transfer of petrol, oil, air, water and other fluids. The importance of fire hose notably for civil defence needs no emphasis. Rubber-insulated wires and cables make a particularly

important contribution to defence, apart from ordinary wiring, for innumerable purposes which defy recording. They are used as control cables for searchlights and anti-aircraft guns, for operating the electrical equipment on naval craft, and in the form of belts around ships for degaussing as protection against mines.

Special rubber pads of every description are employed in tanks and aircraft, to afford protection to the occupants against shock of warfare. Similar products are employed in parachute parts and as accessories to various instruments of war.

It has been disclosed that a four-engined bombing plane requires approximately one ton of compounded synthetic rubber, involving 800 to 1,000 lbs. of the crude material. Of this total, probably 20 per cent. is represented by the linings of the bullet-sealing fuel cells, which must be made from an extremely oil-resistant synthetic rubber such as Hycar OR-15 or the SR-A type. The actual sealing material in the tank wall is made of either natural or an oil-soluble synthetic rubber, such as GR-S. Some of the fuel cells also have an outer jacket of synthetic rubber for protective purposes and synthetic rubber cement is used not only in the original fabrication but also in vital repair work.

Hard synthetic rubber sponge is used to fill in void spaces in wings to preclude the possibility of petrol accumulating from slow leaks and forming a fire hazard. This sponge does not absorb the petrol, since each of the millions of tiny cells in the sponge is totally enclosed by a film of hard, petrol resistant synthetic rubber. This synthetic rubber sponge is also an extremely light material, weighing less than 5 lbs. per cubic foot.

Other somewhat similar applications which require oil-resistant synthetic rubber are bullet-sealing fuel hose, also oil hose and hydraulic hose for various controls. Natural rubber cannot be used in these applications because of the destructive action of petrol, oil and the fluid used in the hydraulic control systems. These liquids have little effect on oil-resistant synthetic rubber. This resistance to the fluid used in hydraulic control systems explains why synthetic rubber is also employed in accumulator bags of which each four-engined bomber has several, including controls for fuel pressure, oil pressure, brakes, propeller pitch, landing gear and similar applications.

Other uses requiring the oil-resistant type of synthetic rubber are diaphragms for carburettors, fuel gauges and various fuel systems and control-system valves. Gaskets, packings and seals for these items as well as for fuel pumps and oil pumps necessitate the use of oil-resistant synthetic rubber.

From the point of view of personal equipment of combatants,

rubber also plays an important part. Rubber boots and shoes are necessary parts of the equipment of soldiers and sailors, special types being used for airmen. Rubber raincoats protect them from the weather, while rubber ground sheets are quite general. Rubber is also an indispensable part of gas-masks, both for military and civil purposes. Nearly every form of naval craft, aircraft, and military vehicles of war use hard rubber accumulator cases for their storage batteries. Pontoon bridges are built from rubber. Rubber dinghies and life jackets are also standard equipment for airmen. The barrage balloon is another familiar article which in great part depends upon the properties of rubber.

Growth in the Use of Rubber. Rubber has been in use for just over a century. Its really important and large-scale application runs parallel with the development of the motor-car, and is also bound up with the growth of the plantation industry in the Far East. The following table illustrates the growth in the consumption of natural rubber over a long period.

TABLE 3. CONSUMPTION OF NATURAL RUBBER

	Tons
1860	1,500
1875	9,000
1890	30,750
1900	48,000
1910	95,000
1915	155,000
1920	295,000

Rubber was necessary for the development of the modern car, the growing popularity of which has in turn greatly enlarged the rubber industry. The modern car contains about 200 different parts made

TABLE 4. CRUDE RUBBER: WORLD ABSORPTION, IN SPECIFIED YEARS, 1925 TO 1940

(*In thousands of long tons*)

Year	United States	United Kingdom	Continental Europe	Other areas	Total
1925	388	30	100	40	558
1930	376	75	185	79	715
1935	491	95	237	113	936
1937	544	114	287	150	1,095
1939	592	123	256	131	1,102
1940	648	147	130	159	1,084

Source: Statistical Bulletin of the International Rubber Regulation Committee.

Table 5. Net Imports of Crude Rubber into Principal Manufacturing Countries [7]

(Long Tons)

	United States †	United Kingdom	France (*h*)	Germany	Canada (*ac*)	Japan (*da*)	Italy	Russia (*ce*)	Australia (*cd*)	Belgium (*d*)	Netherlands	Scandinavia (*abcdf*)	Spain (*g*)	Czechoslovakia (*abcd*)	Total
1919	238,407	42,671	17,685	5,584	6,395	9,753	9,894	75	1,002	3,995	2,771	3,149	2,418	9	343,808
1933	398,365	73,335	61,953	54,120	19,332	66,831	19,341	29,830	13,534	11,166	1,243	7,831	5,520	10,402	772,803
1934	439,172	158,482	49,560	59,330	28,439	69,905	21,398	47,271	9,642	9,115	3,758	12,418	6,900	10,999	926,389
1935	455,758	128,829	51,450	62,899	26,870	57,567	21,880	37,572	9,978	7,593	4,068	11,878	8,140	11,245	895,727
1936	475,359	—2,591	57,032	71,794	27,871	61,223	16,534	30,967	14,109	9,648	2,888	11,236	6,668	8,772	791,510
1937	592,394	92,707	59,871	98,170	36,088	62,311	24,733	30,462	19,164	14,970	4,343	4,680	2,400	13,063	1,055,356
1938	406,343	133,079	59,660	90,200	25,696	45,836	28,170	25,650	11,944	11,309	5,092	16,034	2,400	9,936	871,349
1939	486,348				31,615	42,352			15,426	9,612	7,051				
1940	811,564														
1940:															
Feb.	41,797	7,500	5,000*	....	3,508	5,241	1,500*	2,000*	1,846	694	495	1,200*	200*	....	....
Mar.	58,302	14,200	5,000*	....	3,062	6,057	1,500*	2,000*	1,784	....	627	1,200*	200*	....	....
Apr.	70,135	16,400	5,000*	....	3,096	2,000*	1,500*	2,000*	1,612	....	....	1,200*	200*	....	....
May	50,610	10,000	5,000*	....	3,108	2,500*	1,500*	2,000*	2,128	....	....	1,200*	200*	....	....
June	53,266	9,500	5,000*	....	1,062	3,000*	1,500*	2,000*	1,181	....	....	1,200*	200*	....	....
July	69,496	19,500	5,000*	....	5,112	3,000*	1,500*	2,000*	1,902	....	....	1,200*	200*	....	....
Aug.	72,612	21,250	5,000*	....	4,605	4,500*	1,500*	2,000	2,508	....	....	1,200*	200*	....	....
Sept.	78,306	25,940	5,000*	....	2,743	....	1,500*	2,000*	2,485	....	....	1,200*	200*	....	....
Oct.	74,400	.....	5,000*	....	8,336	....	1,500*	2,000*	590	....	....	1,200*	200*	....	....
Nov.	72,775	.....	5,000*	....	5,451	....	1,500*	2,000*	1,366	....	....	1,200*	200*	....	....
Dec.	97,794	.....	5,000*	....	7,437	....	1,500*	2,000*	721	....	....	1,200*	200*	....	....
1941:															
Jan.	86,541	.....	5,000*	....	6,290	....	1,500*	2,000*	1,065	....	....	1,200*	200*	....	....
Feb.	73,647	.....	5,000*	....	3,770	....	1,500*	2,000*	1,717	....	....	1,200*	200*	....	....
Mar.	86,794	.....	5,000*	....	3,879	....	1,500*	2,000*	3,486	....	....	1,200*	200*	....	....
Apr.	64,521	.....	5,000*	....	2,531	....	1,500*	2,000*	2,326	....	....	1,200*	200*	....	....
May	101,034	.....	5,000*	....	5,596	....	1,500*	2,000*	1,549	....	....	1,200*	200*	....	....
June	64,101	.....	5,000*	....	2,818	....	1,500*	2,000*	1,373	....	....	1,200*	200*	....	....
July	96,658	.....	5,000*	....	4,143	....	1,500*	2,000*	2,003	....	....	1,200*	200*	....	....
Aug.	105,556	.....	5,000*	....	10,683	....	1,500*	2,000*	1,251	....	....	1,200*	200*	....	....
Sept.	81,742	.....	5,000*	....	....	....	1,500*	2,000*	4,392	....	....	1,200*	200*	....	....

a—Including gutta percha. *b*—Including balata. *c*—Re-exports not deducted in monthly statistics. *d*—Including some scrap and reclaimed rubber. *e*—Official statistics of rubber imports by Soviet Russia. *f*—Including Norway, Sweden, Denmark and Finland. *g*—United Kingdom and French exports to Spain except in years prior to 1925. *h*—French imports have been reduced in order to eliminate imports of gutta percha and to reduce to basis of net weight. †—United States imports of guayule are included in this compilation. *—Figure is provisional.

chiefly of rubber. It has been estimated in the United States that an average car contains about 145 lbs. of rubber. It is used in practically every available form as latex, cements, soft rubber, hard rubber, sponge rubber. Every important characteristic of rubber is utilized.

It is absolutely essential to realize that the importance of rubber is entirely due to its physical properties which have been so amazingly developed by the skill of the rubber technologist. Chemical properties play a comparatively minor part. This has an important bearing on the development of synthetic rubber.

TABLE 6.[8] IMPORTS OF NATURAL RUBBER DURING 1946

	Tons
U.S.A.	681,230
U.K.	109,966
France	62,919
Germany	12,513
U.S.S.R.	35,000
Italy	32,500
Other European Countries	89,250
Australia	23,628
Argentine	33,500
Japan	12,500
South Africa	13,000
Rest of World	88,500
Total	1,225,500

It is of interest to view the chief physical properties which give rubber its importance. They may be summarized as follows : [2]

It has great flexing endurance, withstanding considerable distortion without injury.

It has a very high tensile strength which reaches about 30,000 lbs. per square inch at cross-section on break.

Very rapid elastic recovery.

The elongation can be adjusted to almost any desired value over a very wide range.

It has a great range in properties from soft to hard rubber.

Hysteresis provides self-damping effects.

It has a high capacity for absorbing energy.

Its resistance to chemicals is outstandingly good.

It has high resistance to abrasion.

Its high dielectric strength makes rubber a splendid insulator.

It has a high coefficient of friction against nearly all surfaces.

It has excellent water-proofing properties.
It has low permeability to most gases and liquids.
It is a thermo-setting plastic, and is readily moulded.
It is available in a wide range of colours.
It is available in liquid condition as dispersion or cement.

In order to see synthetic rubbers in their true perspective, it is obviously desirable and necessary to make a brief study of the properties of natural rubber.

In considering the different uses of rubber, it is found that at least one, and usually several, of the outstanding properties have caused it to be chosen for any particular purpose. For example, in a motor tyre rubber is used in the inner tube because flexibility and low permeability to air are necessary. It is employed in the tyre carcase because of its outstanding flex resistance, and because it insulates the cotton cords and prevents them from chafing. In the tyre probably no other material than rubber affords the necessary resistance to abrasion, shock absorption, water-proofing, and friction against road surfaces.

Qualities of Synthetic Rubber. It is impossible to make any general comparison of quality as between synthetic and natural rubber. The classes of synthetic rubber have very different properties. It is possible by skilful processing to produce varieties within a given class which possess a fairly wide range of characteristics. For some purposes certain kinds of synthetic rubber are superior to natural rubber, but for other major purposes natural rubber is superior to any synthetic rubber thus far developed. It is to be expected, however, that with further experience synthetic rubbers will be improved and ultimately types may perhaps be produced which are equal to natural rubber even for the uses where the latter is now definitely superior.

The Scope for Synthetic Rubbers. In general the possibilities for the use of synthetic rubber correspond to almost every use of natural rubber ; in many applications where natural rubber is unsuitable synthetic rubbers have additional outlets. No single synthetic rubber has the versatility of rubber. It is in some specialized application that they score. As a result collectively the synthetic rubbers have a marked advantage over natural rubber.

Thus GR-S has been the material employed in the United States to make tyres. It must be admitted that GR-S is not in any sense the ideal material for tyres. It does an effective job. It was selected for largest scale production because it was the most practicable material possible to meet the extremely critical situation.

Similarly, Buna S was the synthetic rubber generally used in Germany for tyres, Perbunan being applied chiefly where resistance to swelling is necessary. Buna S is cheaper to make, and has better adhesive properties than Perbunan, although not equal to natural rubber in this respect. Rubber is used for making the carcases of tyres, while Buna S is used for the tread. These two can be directly bonded, which is not possible with Perbunan and rubber. This lack of adhesive properties is a great disadvantage in tyre construction and similar applications. With the possible exception of neoprene this lack of tackiness is an outstanding defect of almost every synthetic rubber-like material.

The resistance to hydrocarbon liquids is responsible for the wide application of synthetic rubbers in hose and tubing, and in the handling of petroleum products. In oilfields, refineries, tankers, filling stations, and in the car itself petroleum products now are usually transported through hose and tubing made of synthetic rubber and into tanks which are sealed with it. Many other parts in cars which come into contact with oil are being made from one variety or another of synthetic rubber. For use in contact with oils, grease, fats, and so on, synthetic rubber is widely applied. Conveyor belts, industrial tyres, gaskets, and sealing devices are likewise made from synthetic rubber ; soles and heels, aprons, gloves and other garments for use under similar conditions, also come into the same field of application. The great stability of synthetic rubbers towards liquids accounts for their growing use in printers' rolls and blankets, engraving plates, and similar articles. Pipes of spraying equipment for paints and lacquers are also made from synthetic rubbers. According to a fairly recent statistical survey made by the B. F. Goodrich Co.,[5] synthetic rubber can be substituted for natural rubber 769 times out of 1,000 in the mechanical goods field. Since rubber has been in short supply this proportion has become even greater.

There is an ever-growing application of synthetic rubbers in the electrical field. Those with super-electrical properties such as polyisobutylene and the Buna-S type, are superior to natural rubber, and are being used in insulation for wires and cables. For many uses at low voltages, other types such as neoprene, Thiokol, and polyvinyl chloride are also used for insulation. The big field so far has been in the form of sheathing over insulation of natural rubber or other materials. They are often used in this manner to protect rubber from the effects of light, air, ozone, oils, and other deteriorating influences. The low permeability of gases and resistance to sunlight accounts for the growing application of synthetic rubbers in balloons for every purpose. The impregnation of fabrics of every description with synthetic rubbers

possessing better ageing properties than natural rubber has opened up the domestic field of application. For example, umbrellas, raincoats, tablecloths, shower curtains and so on, are typical products which have been made from polyvinyl chloride, possessing in addition to other merits a wide range of colours.

Disadvantages of Rubber. While rubber was unique its properties had to be good enough, but as soon as other elastic materials became available these properties were subjected to closer scrutiny.

The question has been posed as to whether the exceptional versatility of rubber is altogether desirable. For example, what use is outstanding elasticity to an electrical engineer who desires only an insulator? What properties are there in a rubber article of the mechanical type such as a doormat that might make it desirable for use as an eraser? What is the use of the outstanding insulating properties of rubber in a motor tyre or a pair of shoes? The general trend of product development is towards specialization. It is the functional aspect of materials which has become important.

In the case of rubber this has great point, because in spite of the excellent range of properties outlined above, these are unfortunately inevitably accompanied by an almost equally impressive number of serious disadvantages. For example, rubber deteriorates with age; it is attacked by oxygen, ozone and sunlight; minute amounts of such common metals as copper and manganese make it break down rapidly; it is attacked by strong acids; by oils and solvents. Chemically it is extremely reactive owing to its unsaturated character. The common feature of all these deleterious influences is that the elasticity is lost, which is fatal to most vulcanized rubber articles. In many instances the disadvantages of rubber for a particular purpose are in no sense compensated by the many superfluous virtues which do not come into operation.

With the passing of time the conditions under which rubber must work have become more and more strenuous and exacting. They are conditions which involve the poor properties rather than the good properties of rubber. For example, the increased trend towards mechanization of every description calls for contact with oil and petrol under extreme conditions of temperature. Thus the internal combustion engine, involving all these considerations, is the fundamental feature in transport of every description; motor vehicles, aircraft, tanks and shipping. In some of these machines which are used in extremes of climatic conditions, exceptional temperature conditions are superimposed upon the internal heat and solvents present. Moreover, the rubber parts of the equipment must be adequate to withstand

both extremes of heat and cold. Thus in aircraft products rubber parts must be suitable for the low Arctic temperatures and even worse sub-stratosphere temperatures, and yet the same equipment must be able to withstand tropical heat.

There are numerous conditions, notably in the electrical field, where ozone is present which has a disastrous effect on rubber, unless adequately protected. In many industries corrosive conditions abound in such a form that ordinary rubber compositions cannot withstand them. The numerous new industries have their own specialized requirements far in excess of the old standards for which rubber was regarded as an unsatisfactory but unavoidable expedient. Those consumers who have been dissatisfied with the deficiencies of rubber have accepted synthetic rubber with satisfaction ; they have been willing to pay the high price when this applied. In order to satisfy this demand rubber manufacturers have become used to handling synthetic rubber.

It should, however, be fully realized that most manufacturers were using large quantities of synthetic rubbers against their own wishes. They would much rather use natural rubber if it were available. This trend is already quite clear.

Although this is indisputably the case in Great Britain, it is by no means certain that it applies any longer in the United States.

It is unnecessary to stress at any length the importance of non-inflammability which is so essential for many purposes, especially under war conditions.

It is the failure of rubber to meet these requirements that has lent urgency to the search for synthetic substitutes. It has supplied the thin end of the wedge, and materials which have proved superior for such applications have met with ready demand even at far higher cost. Thus the immediate demand for neoprene and Thiokol when they appeared in 1931 came from the automobile industry.

Advantages of Synthetic Rubbers over Natural Rubber. Before the present situation of shortage of natural rubber arose, synthetic rubbers achieved popularity in spite of their high cost, because of possessing superior properties. The outstanding property that nearly all possessed was their resistance to the influence of solvents, particularly petroleum products. The only notable exceptions are Buna S and butyl rubber which, however, are very good in nearly every other respect. In general, it is not actual swelling which is a serious disadvantage so much as the loss of tensile strength, which almost invariably accompanies it. It is found that the tensile strengths of most synthetic rubbers are less affected even when the amounts of swelling are comparable with rubber. Another feature is that in general more

material is extracted from rubber mixes by solvents than from synthetic compositions.

Second only to the resistance to swelling is the resistance of synthetic rubbers to deterioration or ageing. This applies to nearly all the conditions which undermine the utility of natural rubber. These conditions include exposure to oxygen, to ozone from electric discharges, to ultra-violet light, or to high temperature. In this connection most of the disadvantages of rubber are explained by its unsaturation. Some credence is lent to this idea by the fact that saturated materials such as polyisobutylene and polyvinyl chloride are exceptionally resistant. Their flex resistance is also generally superior, and in some cases, e.g. butyl rubber, incomparably so.

Synthetic rubber compositions in general offer greater obstruction to the passage of liquids and gases than do rubber compounds. To some extent this is attributed to the absence of materials such as proteins and carbohydrate products which are present in rubber. Differences in structure also undoubtedly contribute to this.

Synthetic rubbers are far less permeable to gases, which is a factor of very great importance during the war.

GR-S is approximately about the same as natural rubber in this respect, but Perbunan is at least twice as good. Materials such as neoprene and the polyvinyl chloride products have very great resistance to burning, largely due to their content of chlorine. This is a great advantage over rubber.

The position can be briefly summarized as follows:

Natural rubber is superior in :—

1. Processing properties.
2. Extensibility (in most cases) and elasticity.
3. Resilience (i.e. low hysteresis loss).
4. Maintenance of elastic properties at low temperature (in most cases).
5. Tear resistance.
6. Cutting resistance.
7. Rapid elastic recovery.

Synthetic elastic materials are superior in :—

1. Resistance to deterioration by oils and organic solvents.
2. Resistance to oxidation or ageing:
    (*a*) Induced by actinic rays (sunlight, etc.).
    (*b*) Induced by heat.
    (*c*) Induced by strong oxidizing agents or metals.
3. Lower permeability to gases and liquids.

According to Konrad,[6] Buna S in tyres has an advantage of 25 per cent. better abrasion resistance. Electrical properties of certain of the synthetic rubbers such as polyisobutylene, butyl rubber, and Buna S are superior to those of natural rubber. In other materials such as neoprene, Perbunan, and polyvinyl chloride, there are polar groups present which have an adverse influence generally on electrical properties.

It is the case that synthetic rubber-like materials are in general more difficult to process than natural rubbers. But it is a noteworthy fact that the art of compounding natural rubber has only really seriously been carried forward during the last twenty years. Compounding of synthetic materials has only a history of a few years. In the case of the oldest commercial type—neoprene—with a history of seventeen years, there are now very few difficulties in processing. Other types have a shorter history and are not quite so far advanced. With the heavy pressure of intensified world-wide effort great advances can be anticipated during the next few years.

So far as suitability of synthetic materials for the major application—tyres—is concerned the most critical survey has been favourable. According to evidence obtained by the technical advisers to the Baruch Committee, GR-S will give certainly 90 per cent. of the wearability obtainable from rubber. It is quite satisfactory for use in inner tubes. They concluded that a certain amount of crude rubber was necessary in making up carcases and sidewalls of tyres. However, not more than 20 per cent. of a heavy Buna-S tyre would need to be crude rubber.

These opinions have since been substantiated by the performance of many millions of tyres both for military and civilian purposes. There are faults—indeed serious faults—but the fact remains that satisfactory tyres can be made.

There is another factor of outstanding importance—change in design. The chief cause of failure of synthetic rubbers in tyres has so far been the high heat build-up, with its adverse effect on the cotton in the tyre carcase and sidewalls. It has been shown that rayon carcases will withstand much higher temperatures—in fact for heavy-duty tyres there is a trend for rayon to replace cotton for this reason. Thus rayon is said to be as effective at 105° C. as cotton is at 75° C. It is considered very likely that the use of rayon together with synthetic rubbers may greatly alter the situation, and may overcome some of the difficulties now being experienced.

Killiffer[5] has admirably brought the matter into true perspective.

Tyre builders are already exploring with considerable success the possibilities of the several varieties of synthetic rubbers now available and of new

types of strengthening fabrics. Already their investigations have demonstrated that the accustomed technology of plantation rubber fails to bring out the full potentialities of the synthetic products. Tyres made of synthetics by the accustomed rubber methods reveal surprising shortcomings. The heat produced in the side wall during flexing is, for example, substantially greater than in rubber tyres. For the present, little can be done about that since new moulds and fabricating equipment are and will remain unobtainable until the war's burden on metals is eased. When rubber fabricators have an opportunity to revise both their methods and their machines, the answers to many present problems will be easily found. Tyre builders in the past have developed their methods by degrees. The historical development, coupled with the necessity for frequent removal of damaged tyres for repair, has given us our present design. However, when designers are again able to use any materials they fancy without limitation, the possibilities become enormous. For example, the techniques of self-sealing gasoline tanks and bullet-proof tyres suggest the building of tyres that cannot be punctured. The extraordinary wearing qualities of some of the synthetics and their extreme resistance to air, ozone, sunlight, and other factors in rubber failure through age point directly to future tyres that may, not unreasonably, be expected to last as long as the car which they carry. Stronger fabrics of rayon, nylon, steel, and glass fibres provide obvious answers to the problem of blowouts and will permit economies through reducing the thickness of the tyre. Already test tyres of synthetics are reported to have lives equal to natural rubber tyres and some hope is held for lives as great as 100,000 miles. Thus no difficulty is apparent in building the tyre as an integral part of the wheel. The air cushion can even be largely enclosed in the wheel itself, reducing the quantity of synthetic required without sacrificing the over-all resilience of the assembly.

The Importance of Vulcanization. Considering rubber as a raw material, it owes its important position to two main causes: (1) the physical properties possessed by soft vulcanized rubber, and (2) the plastic characteristics of masticated unvulcanized rubber which makes it easily amenable to factory operations. It can be worked and manipulated in any desired manner. The fundamental change caused by vulcanization is of the greatest possible importance. It is a change in condition usually affected by heating with sulphur, and is best defined by contrasting the difference in physical properties. The properties of unvulcanized rubber: [2]

(*a*) Low tensile strength		(*a*) High tensile strength
(*b*) Limited elasticity		(*b*) Extensive elasticity
(*c*) Low recovery		(*c*) High recovery
(*d*) High retentivity		(*d*) Low retentivity
(*e*) High flow	Change to	(*e*) Low flow
(*f*) Narrow temperature range		(*f*) Wide temperature range
(*g*) Plasticity-thermo-plastic		(*g*) Non-plasticity
(*h*) Solubility		(*h*) Lack of solubility
(*i*) Tack		(*i*) Lack of tack

Thus consider a normal rubber composition before and after vulcanization. Before vulcanization it is easily pulled apart, and if much extended does not tend to retract, although under impact the rebound is considerable. When heated it becomes softer and more plastic, being easily formed into any desired shape. If cooled below 0° C. it becomes stiff and boardy. It is readily soluble in hydrocarbon solvents. When two fresh surfaces are pressed together they adhere and become practically integral. This property of tack is extremely valuable in manufacturing operations.

After vulcanization (or " cure " as the process is technically known) rubber is tough and strong, and even after considerable distortion returns rapidly to its original shape. There is little tendency to flow, and hardly any tack. Hydrocarbon solvents make it swell, but it will not dissolve it. These characteristics do not vary greatly from − 40° C. to well above 100° C. This comparison illustrates how the elastic character of rubber is developed during vulcanization.

The general nature of the synthetic materials is often described by one of the three following terms : " vulcanizable ", " thermosetting " or " thermoplastic ". Each of these may be briefly defined as follows : vulcanization as in rubber, is a process by which the synthetic is changed from a thermoplastic substance, soluble in many organic solvents and susceptible to marked physical and chemical alteration within the range of ordinary atmospheric temperature, to a new material which is highly elastic, insoluble in most organic solvents and relatively insensitive to changes over a considerable temperature range. This change is brought about by the reaction, under the influence of heat, of the material with some added chemical, such as sulphur, zinc oxide, magnesia or litharge.

A thermosetting synthetic resin will undergo a similar change, but this change is usually brought about by the action of heat alone, and the products are seldom highly elastic, although in some instances sufficiently so as to warrant their consideration as synthetic rubber. The original physical and chemical properties of thermoplastics are not usually appreciably affected by changes in ordinary atmospheric temperature and these materials do not exhibit a permanent change in properties as do the vulcanizable and thermosetting types. Here the action of heat is merely to soften the material in order to facilitate extrusion or moulding and to relieve internal stresses. In other words, the same material may be milled or extruded repeatedly, whereas curing (heat treating) of the vulcanizable or thermosetting types renders the material non-thermoplastic and it can therefore not be re-milled or re-extruded.

The Status of Thermoplastics in the Synthetic Rubber Field. There are many thermoplastic materials having the rubber-like properties of soft vulcanized rubber. They tend to be applied more and more for products previously made of rubber. They differ fundamentally from rubber and elastomers (i.e. synthetic rubbers related to rubber) inasmuch as there is no chemical change from the plastic to the elastic state. That being the case there is a definite limiting temperature beyond which the characteristic plastic flow becomes appreciable. As Von Rosenberg [10] has pointed out, a satisfactory commercial material must be very plastic at the temperature at which it is processed, but it must have little plasticity, but much elasticity in the temperature range at which it is to be utilized. The ideal would be a material whose plasticity was nil during the working range but which at the top limit changed within a few degrees to the soft plastic state for processing. Rubber and elastomers once set or vulcanized no longer have the physical defects inherent in the plastic state.

The thermoplastics which have or can acquire rubbery properties during the normal working range of temperatures may be conveniently grouped as:

(1) Materials having rubber-like properties such as polyisobutylene, acrylic acid esters, polyvinyl butyral, etc.
(2) Materials which are intrinsically hard and whose latent rubber-like properties are brought out by addition of plasticizers. These include: polyvinyl chloride, polyvinyl chloride-acetate, polyvinyl alcohol, etc.

It is interesting to note that the plasticizing effect is specific. Only certain plasticizers are effective. These are sometimes called elasticizers—an ugly word, but one whose meaning is quite clear.

There are, in addition, alkyd-condensation products which, however, do not really enter the rubber field and are not truly reversible thermoplastics. A case can be made out for cellulose ethers, e.g. benzyl cellulose and ethyl cellulose. At one time a great deal was heard about ethyl rubbers, based on ethyl cellulose.

It is interesting to review in brief some of the outstanding features of rubber-like materials in relation to natural rubber.

Rubber reinforced with channel black still has the highest tensile strength to be obtained with elastic materials. Several elastomers are not far behind in this respect. But in pure gum mixes, or those containing inert fillers, rubber is already equalled and surpassed by elastomers, and by thermoplastics such as polyisobutylene and plasticized polyvinyl chloride.

Polyisobutylene and butyl rubber have higher elongations at break than rubber, which is also equalled by elastomers such as GR-S, neoprene, Perbunan, etc.

Rubber and elastomers do not tend to undergo considerable permanent deformation under prolonged stress, whether in extension or compression. The thermoplastics all have a pronounced tendency to flow or " creep ", the effect being perhaps least pronounced in polyvinyl chloride, varying with plasticizer content, etc.

In resilience or rebound, rubber is as yet unequalled even by the elastomers.

But as Semon [9] has said : " The advantages in the use of synthetic rubber lie largely in the future. . . .

" The real future for synthetic rubber lies in its ability to do a better job or perform a function which can be performed by no other material."

Rubber Practice and Plant the Same throughout the World. Every industrial country in the world has a rubber-manufacturing industry. The equipment in every manufacturing establishment throughout the world is identical in principle, variations being largely a question of size, capacity, and newness. The procedure is likewise similar. Raw rubber, either crêpe or smoked sheet, is masticated or broken down on open rolls or in an internal mixer, the Banbury type being the most widely used. When it has been reduced to a plastic mass it is compounded, all the necessary ingredients being added on the mill or in the mixer.[1]

It is interesting to note in connection with processing that the property of plasticity is of more fundamental importance than elasticity. During all manufacturing processes the important property is plasticity. Elasticity is required only in the final product, when vulcanization virtually eliminates plasticity.

Thereafter the processing depends upon the nature of the product being made. Compounded rubber may be calendered or extruded, or it may be moulded. It may be frictioned or skimmed on to fabric, or it may be fabricated in many ways ; this flexibility in use is one of its most valuable properties. To a great extent it is dependent upon the unique tackiness of rubber. It may also be converted into doughs or taken up into solutions and used in these forms.

The plastic rubber compound is then formed either in a mould, or by assembling, or by extrusion, and is then vulcanized either in a press or under open steam pressure, or in air, or by low temperature methods.

The important point which is brought out in this description is

that all the plant required to handle rubber exists in very large quantities. A great deal of capital is sunk in this plant. Large numbers of skilled personnel are already available. Consequently it is essential, irrespective of any other merits that it may possess, that any substitutes for rubber should be suitable for handling on the same equipment. Failing this, it is hopeless to expect any rapid expansion in its use.

Other industries in which rubber is extensively used, and which have special equipment to handle it, are interested from the same angle. Obviously the highly specialized equipment of a tyre factory cannot be scrapped. It is for the new material to conform to the equipment. The same applies to plant for making boots and shoes. Another outstanding example is the longitudinal machine which is the backbone of insulated wire manufacture. Any new material suggested for the same purpose must be suitable for application on this machine. Many other examples can be brought to mind.

REFERENCES

[1] BARRON, *Modern Rubber Chemistry*, Hutchinson, London, 1947.
[2] Baruch Report—Appendix : *Chemistry of Synthetic Rubber*, Washington, 1942.
[3] CADWELL, MERRIL, SLOMAN and YOST, *Ind. Eng. Chem.*, 1941, **33**, 370.
[4] GARVEY, ALEXANDER, KING and HENDERSON, *Ind. Eng. Chem.*, 1941, **33**, 1060.
[5] KILLIFFER, *Ind. Eng. Chem.*, 1944, **36**, 1139.
[6] KONRAD, *Kautchuk*, 1937, **13**, 2.
[7] *Rubber Age* (N.Y.), 1942, **50**, 310.
[8] *Rubber Statistical Bulletin*, Feb. 1948.
[9] SEMON, *Ind. Eng. Chem.* (*News*), 1943, **21**, 1619.
[10] VON ROSENBERG, *Proc. Rubber Conference*, London, 1938, p. 450.

CHAPTER 2

ECONOMICS OF SYNTHETIC ELASTIC MATERIALS

UNTIL 1942 the synthetic rubber position appeared to have fallen into a well-defined pattern. It was common knowledge that countries such as Germany, and the U.S.S.R. had proceeded with the synthetic rubber production to the virtual exclusion of the natural product. In contrast, United States production although small was geared to commercial demands, neoprene and Thiokol being well-established commercial materials. Until the rubber-producing areas of the Far East were overrun by the Japanese early in 1942, the position was that Russia and Germany already had large-scale synthetic rubber-producing industries ; the United States production was relatively small. The position is now quite changed.

With nearly all sources of natural rubber in enemy hands synthetic rubber almost overnight became a major factor in world affairs. Sources of supply of more than a million tons of natural rubber per annum had passed out of the hands of the chief consumers. All preconceived ideas were swept away by the rush of events. The tolerant acceptance of apparently expensive luxuries changed into an urgent insistence on their necessity. Criticism of the " ersatz " materials of the totalitarian countries and Russia was completely stilled. Although natural rubber had disappeared, the demand for it had become even greater and more urgent. It was necessary to consider synthetic rubber against the dramatically changed background of a shortage of rubber available to the leading rubber consumers. The consequence was a synthetic rubber production scheme in the United States which aimed at the enormous total of 1,100,000 tons per annum. The programme was carried forward with incredible speed. This objective had been virtually attained by the time natural rubber once again became available. A large proportion of the American production capacity remains. The implications are serious and inescapable.

Before the war spread to the Far East synthetic rubber was an insignificant competitor of natural rubber. It had indeed become something of a bogey to rubber growers. For the last fifty years it had been a somewhat abstract long-distance threat to them, but in recent years it had become a definite tangible reality which had to be faced. The full realization finally crystallized after the loss of the rubber-

Table 7. Exports of Crude Rubber from Principal Producing Countries [18]

(Long Tons)

	British Malaya: Gross Exports	British Malaya: Imports	British Malaya: Net Exports	Ceylon	India & Burma	Sarawak	British North Borneo	Thailand	Indo-China	Netherland Indies: Java & Madura	Netherland Indies: Sumatra E. Coast	Netherland Indies: Other N.I.	Amazon Valley	All Other	World Total
1923	252,016	70,432	181,584	39,971	6,416	5,705	4,237	1,718	5,067	32,930	46,344	57,822	16,765	7,856	406,413
1933	573,412	167,377	406,035	63,351	4,527	10,874	7,555	7,765	18,394	73,851	91,861	149,659	9,883	2,737	846,312
1934	677,361	211,803	465,558	79,746	10,492	17,233	11,103	17,545	20,170	87,400	112,058	175,470	8,903	2,985	1,008,663
1935	590,319	174,652	415,667	54,316	13,968	19,465	8,885	28,327	28,816	57,488	78,325	139,297	11,275	8,745	864,574
1936	520,286	167,799	352,487	49,692	14,724	21,243	8,177	33,702	40,782	61,307	84,577	152,205	14,193	11,466	845,431
1937	681,638	213,446	468,192	70,353	17,015	25,922	13,213	5,551	43,399	84,085	139,632	207,863	15,576	13,063	1,133,864
1938	526,911	156,101	370,810	49,528	15,178	17,792	9,512	41,080	58,518	57,526	94,501	145,909	14,618	12,920	887,892
1939	553,324	177,851	375,473	61,026	15,881	24,014	11,864	41,266	65,140	72,786	117,791	181,272	13,892	22,224	1,002,629

	British Malaya [1]	N.E.I.	Ceylon [2]	India & Burma [2]	Sarawak	North Borneo	Thailand	Indo-China	Oceania	Africa [3]	Liberia	South America	Mexico (Guayule)	Grand Total
1940	540,417	536,74c	88,894	23,317	35,166	17,623	43,940	64,437	2,267	10,103	7,223	17,601	4,106	1,391,834
1940:														
Aug.	45,872	45,078	8,139	1,332	2,640	1,593	4,545	7,337	285	800	308	1,233	327	120,729
Sept.	58,892	44,009	9,985	1,319	2,404	1,743	3,247	9,303	100	800	323	1,295	200	133,715
Oct.	52,767	50,139	8,127	1,841	2,564	1,693	3,355	2,082	200	800	600	1,860	200	126,228
Nov.	36,045	37,387	5,623	2,626	3,360	1,130	3,463	6,715	200	800	600	1,500	200	99,649
Dec.	56,263	35,325	10,700	3,405	3,520	1,028	5,343	9,000	200	600	813	1,427	392	128,216
1941:														
Jan.	37,804	58,593	7,859	1,486	2,445	2,085	2,137	9,058	333	667	750	2,103	288	125,608
Feb.	27,115	42,091	4,332	1,421	2,922	1,686	4,137	1,995	96	854	828	1,814	414	89,705
Mar.	56,651	53,233	6,073	1,770	3,726	1,154	5,712	6,286	117	636	958	2,835	355	139,506
Apr.	40,590	48,915	6,985	1,661	3,118	2,175	4,271	....	263	864	750	2,009	423	112,024
May	53,062	48,099	7,638	1,831	3,849	1,237	1,841	6,225	156	800	180	1,080	334	126,332
June	51,247	48,496	8,925	1,056	3,195	986	2,831	7,318	200	800	919	1,510	250	127,733
July	53,373	53,429	7,387	939	3,799	1,803	3,614	3,445	200	800	750	1,253	250	131,042
Aug.	46,404	51,890	9,081	725	3,086	1,812	4,852	6,496	200	800	750	1,288	250	127,634
Sept.	70,598	65,496	6,706	145	2,495	1,371	6,524	8,000	200	800	750	1,421	250	164,756

[1] Including Brunei and Labuan; figures shown represent rubber which has actually been shipped and include rubber from the free stocks in Singapore and Penang. [2] Exports of domestic produce. [3] Exclusive of Liberia. Notes: Figures shown prior to 1940 were furnished by the United States Department of Commerce. Figures since 1940 were furnished by the International Rubber Regulation Committee, which accounts for the difference in the principal producing countries shown. Many figures for current months are provisional only and are later revised when more definite statistics are available. Therefore, it is suggested that figures from the most recent issue should be taken as more reliable.

growing area. Now of course the position has changed considerably, so that synthetic rubber is no longer insignificant as a competitor of natural rubber.

The position was one which showed up an economic anomaly. Hitherto it had been the custom to refer to a material being in short supply when the price of that material was high. In a situation of absolute shortage, price is of little consequence. In such circumstances synthetic rubber is on an equal footing with the natural material. For it is an elementary fact that no matter what rubber costs, large tyre manufacturers must have a steady flow of rubber into their factories.

We were in an interim period during which consumers of natural rubber could continue only by effecting economies in its use, and by eking out their stocks. By the time these stocks were running low, synthetic rubber will be coming forward in ever-growing volume with the definite object of replacing natural rubber. From the quantitative angle this has been attained. The names of various forms of synthetic rubber, such as neoprene, Thiokol, and GR-S are almost household terms in the United States.

With the end of the war in the Far East a complete change has come over the situation, so that at the time of writing Malayan output has already surpassed the pre-war figures. Production in 1946 was estimated at 646,362 tons, which was a record. The Netherlands East Indies have not recovered to anything like the same extent. Nevertheless, world production in 1947 was estimated at 1,230,000 tons. The recovery in natural rubber production produced still another dramatic change in the situation. Because now there was the early prospect of plenty of natural rubber and also plenty of synthetic rubber—an unprecedented situation.

The Future of Rubber. The misgivings which existed regarding the future of natural rubber have been allayed. The plantations were recovered in comparatively good condition. Renewal of production has been rapid. There is no longer any reason to expect that synthetic rubbers will completely replace natural rubber.

Rubber does a magnificent job in the form of tyres, which account for about 75 per cent. of requirements. Now that more normal conditions prevail, the perspective has altered, and the questions of price and performance have become once again as important as availability.

War conditions provided a favoured milieu for synthetic rubber production, particularly in the United States. The time factor enabled many of the unknown aspects such as bulk production, methods of applications, sources of raw materials, costs, and so on, to be sorted

out. So that to-day both synthetic rubbers and natural rubbers find ready markets. The demand exceeds the supply and so far there is no question of real competition. The following figures illustrate this.

Estimates for 1946 of exports of natural rubber from producing territories are as follows:

	1947 (tons)	1941 (tons)
Malaya	646,362	575,000*
N.E.I.	260,000	635,981
Ceylon	89,000	102,351
Indo-China	37,500	49,446
Sarawak	36,750	45,000*
India	16,500	70,000*
Other Asia	70,000	1,000*
South America	29,000	13,680
Central America	4,000	4,975
Africa	40,000	16,941
Oceania	1,000	1,394
	1,230,000	1,510,000*

Estimated or partly estimated.

Total Consumption. Estimated world consumption of natural rubber during 1947 was 1,082,500 tons.

Collyer has recently quoted the following estimates for 1947, 1948 and 1949.

ESTIMATED WORLD RUBBER PRODUCTION, CONSUMPTION AND STOCKS IN LONG TONS

Crude Rubber

	1947	1948	1949
Stocks, 1st of Year	920,000	1,050,000	1,200,000
Production	1,230,000	1,350,000	1,450,000
Total available	2,150,000	2,400,000	2,650,000
Consumption	1,100,000	1,200,000	1,250,000
Stocks, End of Year	1,050,000	1,200,000	1,400,000

(Including Government Stocks.)

Man-Made Rubber

	1947	1948	1949
Stocks, 1st of Year	140,000	70,000	80,000
Production	560,000	450,000	400,000
Total available	700,000	520,000	480,000
Consumption	630,000	420,000	400,000
Stocks, End of Year	70,000	80,000	80,000

World output of synthetic rubber during 1946 amounted to 806,563 tons, compared with 900,525 tons in the peak year 1944.

World consumption of synthetic rubber in 1946 is estimated to have totalled 910,000 tons, of which the U.S.A. consumed 756,628 tons.

The position of GR-S in the United States is so well established that a price differential of a few cents a pound would cause heavy consumption of GR-S.

The Economic Background of Rubber and Synthetic Rubber. The search for synthetic rubber is almost as old as the rubber industry. The intensity with which it has been carried on has varied with the price of natural rubber, slackening when the price was low, and becoming intensified when the price was high. It is only since 1925 that work on synthetic rubber has become virtually independent of the rubber market. There are many economic factors which have contributed considerable pressure towards the development of synthetic rubbers. They are all well worth close consideration.

Widely Fluctuating Price of Rubber. The fluctuating price of rubber has had a profound effect on the search for synthetic substitutes. The creation of intolerable commercial conditions supplied a great urgency. For large manufacturers, notably the American companies, there has never been any sense of security. It was equally unsatisfactory to them to have rubber at about 6*s.* per lb., as in 1925, as to have it as low as 1½*d.* per lb., as in 1932. They desired a stabilized price for the commodity. Appreciable rises and falls in the price were equally disastrous, since changes in the prices of their tyres and stocks could not follow with equal rapidity, and large sums had to be written off.

When from a top price of about 6*s.* per lb., in 1925, rubber fell to 1½*d.* per lb. in 1932, the big American rubber companies in particular were very hard hit. In order to safeguard themselves they had to buy rubber all the way down. For example, it has been stated that the General Rubber Company [12] had by 1934 written off 50 million dollars. It was these constantly recurring difficult economic situations which have been a major factor in the search for synthetic rubber. During the last fifteen years every large United States rubber firm has had a long-term programme in operation with this object in view.

One angle on the synthetic rubber position has been that no matter how dear it was, it established a definite ceiling for the price of rubber, which previously did not exist.

The Influence of Restriction upon Synthetic Rubber Development. The Stevenson Restriction Scheme started in 1922. Britain then controlled two-thirds of the world's output of natural rubber. Production was cut very drastically in order to bring the price up from 7½*d.* per lb. The process went on, until in 1925 rubber reached 6*s.* per lb. Then there was a fearful drop, due to the fact that the Dutch growers, outside the scheme, began to flood the market with rubber from Sumatra. The Stevenson scheme died in 1928, discredited.

Table 8. Rubber: High, Low, and Average Yearly Prices,[a] 1910–1943

(In cents per pound.)

Year	Highest price	Lowest price	Average
1910 . . .	288·0	141·0	206·6
1911 . . .	184·0	114·0	141·3
1912 . . .	140·0	108·0	121·6
1913 . . .	113·0	59·0	82·0
1914 . . .	93·0	56·0	65·3
1915 . . .	79·0	58·5	65·7
1916 . . .	102·0	55·0	72·5
1917 . . .	90·0	52·0	72·2
1918 . . .	70·0	40·0	60·2
1919 . . .	57·0	38·5	48·5
1920 . . .	56·5	16·0	35·9
1921 . . .	21·3	11·5	16·5
1922 . . .	27·6	13·6	17·5
1923 . . .	35·6	25·3	29·5
1924 . . .	38·5	18·5	26·2
1925 . . .	112·0	35·0	72·5
1926 . . .	85·5	36·0	48·5
1927 . . .	41·5	33·0	37·7
1928 . . .	37·5	16·5	22·5
1929 . . .	24·4	16·1	20·5
1930 . . .	15·8	8·1	11·9
1931 . . .	8·2	4·6	6·1
1932 . . .	4·5	2·7	3·4
1933 . . .	8·8	2·9	5·9
1934 . . .	15·5	9·9	12·9
1935 . . .	13·2	11·4	12·3
1936 . . .	20·0	14·9	16·4
1937 . . .	24·1	14·6	19·4
1938 . . .	16·9	11·6	14·7
1939 . . .	21·5	15·8	17·7
1940 . . .	22·1	19·1	20·1
1941 . . .	23·1	19·9	22·4
1942 . . .	22·5	22·5	22·5
1943 . . .	22·5	22·5	22·5
1947 . . .	—	—	25·75

[a] New York prices for plantation ribbed smoked sheets.

Source: *Commodity Yearbook*, 1941; Statistical Bulletin of the International Rubber Regulation Committee, 1935; *Rubber Age*, various issues; U.S. Department of Commerce.

But one of its unexpected effects was the re-birth of synthetic rubber activity.

The folly of extorting an absurdly high price for rubber as a stimulant to the production of synthetic rubber is fully demonstrated by the experience of the German I.G. Farbenindustrie. From the end

TABLE 9. RUBBER: UNITED STATES PRODUCTION AND CONSUMPTION IN SPECIFIED YEARS, 1925 TO 1946

Year	Production				Consumption			
	Crude natural	Synthetic	Reclaimed[a]	Total	Crude natural	Synthetic[b]	Reclaimed[a]	Total
1925	[c]	[c]	67,994	67,994	388,000	[a]	75,350	463,350
1930	[c]	[c]	82,203	82,203	375,735	[a]	84,425	460,160
1935	[c]	369	65,948	66,317	491,544	285	64,635	556,464
1937	[d] 62	1,101	99,231	100,394	543,600	1,056	89,100	633,756
1939	[c]	1,994	102,298	104,292	592,000	1,951	93,501	687,452
1940	[c]	2,940	115,281	118,221	648,500	2,904	103,387	754,791
1941	[c]	12,356	150,811	163,167	775,000	9,626	138,177	922,803
1942	—	26,385	156,750	183,135	376,800	20,365	140,250	537,415
1943	[d] 473	[e] 234,244	167,200	401,917	317,600	170,900	160,050	648,550
1944	—	—	—	—	144,113	566,670	251,083	961,866
1945	—	—	—	—	105,429	693,580	241,036	1,040,045
1946	—	—	—	—	277,562	756,628	275,497	1,309,687
1947	—	—	—	—	562,661	559,670	288,395	1,710,722

[a] Rubber content (taken as 55 per cent. of the weight of reclaimed rubber).
[b] Sales.
[c] Not available; known to be negligible.
[d] Guayule.
[e] United States and Canada.

Source: Rubber Manufacturers' Association, Statistical Bulletin of the International Rubber Regulation Committee, Commodity Exchange statistical supplement, Office of the Rubber Director, War Production Board.

TABLE 10. PERCENTAGES OF BASIC QUOTAS, AS FINALLY FIXED BY THE INTERNATIONAL RUBBER REGULATION COMMITTEE FOR EACH QUARTER YEAR, 1935 TO 1941

Quarter	1935	1936	1937	1938	1939	1940	1941
1st quarter . .	75		75	70	50	80	100
2nd quarter. .	(75) 70	60	80	60	50	80	100
3rd quarter . .	(70) 65	65	(85) 90	45	(55) 60	85	100
4th quarter . .	(65) 60		90	45	(60) (70) 75	90	120
Average for year	$67\frac{1}{2}$	$62\frac{1}{2}$	$83\frac{3}{4}$	55	$58\frac{3}{4}$	$83\frac{3}{4}$	105

Source: Commodity Year Book, 1941, citing the International Rubber Regulation Committee.

of the last war until 1925 they took no further interest in the synthetic rubber field, an activity in which one of the subsidiary companies, the Bayer concern, had always taken a leading part. But at the peak of the Stevenson Restriction Scheme, commercial prospects became very bright for synthetic materials, and consequently they re-entered the field. The same considerations prompted chemical concerns such as Du Pont de Nemours to examine the possibilities of materials which possessed rubbery properties. The financial prospects justified the expense of large-scale long-term research work.

In recent years there has been a more successful method of restriction. The International Rubber Regulating Committee included Dutch and French representatives as well as British, and began to function in 1934. It has put up a very creditable performance, keeping rubber at a reasonable level by maintaining rubber production in line with rubber consumption. The great drawback was the fact that the greatest rubber consumer in the world—the United States—had no

TABLE 11. RUBBER: BASIC QUOTAS FOR TERRITORIES COVERED BY THE INTERNATIONAL RUBBER REGULATION AGREEMENT, IN SPECIFIED YEARS, 1934 TO 1943

(In long tons)

Territory	1934 [a]	1936	1938	1940	1943
Malaya [b] . . .	504,000	569,000	602,000	642,500	651,500
Netherlands Indies [c]	352,000	500,000	540,000	640,000	651,000
Ceylon	77,500	80,000	82,500	107,500	110,000
India	6,850	12,500	13,000	17,750	17,750
Burma	5,150	8,500	9,250	13,750	13,750
North Borneo . .	12,000	14,000	16,500	21,000	21,000
Sarawak	24,000	30,000	32,000	43,750	44,000
Thailand . . .	15,000	40,000	40,000	55,300	60,000
	996,500	1,254,000	1,335,250	1,541,550	1,569,000

[a] The basic quotas were tabulated on an annual basis, and the percentages exportable June 1 to December 31, 1934, were reckoned on seven-twelfths of the base figures.

[b] Straits Settlements, Federated Malay States, Unfederated Malay States, and Brunei.

[c] The basic quotas originally assigned to the Netherlands Indies for the years 1934–38 were 352,000; 400,000; 443,000; 467,000 and 485,000. The higher figures of the table for 1936 and 1938 were agreed upon by a protocol of May 22, 1936.

Source: Text of International Rubber Regulation Agreement as revised in 1938. See League of Nations Treaty Series, vol. 196, 1939, p. 441. The Agreement of 1934 as registered in 1936 appears in vol. 171, p. 203.

official say in the deliberations, although its advice was sought and acted upon. Nor were other large consuming countries, such as Germany and Russia, represented. It is to be noted that these countries form the vanguard of synthetic rubber producers.

Centralized Production. Although the centralized location of the rubber plantations has been conducive to economic production, it has had grave disadvantages which are now all too apparent. Practically the whole of the industry (some 90 per cent.) was located in and around Malaya and the Dutch East Indies. In this area there were some 8,942,000 acres planted with rubber trees, of which 8,000,000 acres were bearing.

The average daily yield of a *Hevea* tree has been calculated at 1½ ounces, according to Crane,[9] giving an annual yield of 5 lbs. per tree for a tapping season of 140 days.

This meant that the United States, consuming more than half of all rubber produced, had to have rubber transported 12,000 miles, taking two months to arrive. This was a most unsatisfactory position in ordinary times ; it became precarious when Britain and Holland became involved in war, and utterly disastrous when Japan took a hand. Considering one minor aspect of rubber activity, the transportation of large amounts of water (in the form of latex) across such vast distances was also manifestly absurd.

Other Sources of Rubber. Rubber growers occupied a position of almost complete monopoly. British and Dutch growers could dictate their own policy, a state of affairs which had serious repercussions on American industry, since the entire American economy was based upon the motor-car, in turn dependent on the tyre. This monopoly extended so far that even when United States firms were able to purchase plantations, e.g. in Sumatra, they had to conform to the regulations which generally applied, and could only produce up to their quotas. Among other areas the United States Rubber Co. had 135,000 acres in Sumatra, while Goodyear Rubber Corporation owned 550,000, plus experimental areas in Panama, Costa Rica, and Philippines. Firestone Tyre Co. have 110,000 acres in Liberia. The B.F. Goodrich Co. have never gone in for rubber growing, having for many years believed in the inevitability of synthetic rubber. Consequently they have utilized resources, that others have sunk into plantations, for the development of synthetic rubber, with considerable success, e.g. first with Koroseal and Ameripol and then with Geon and Hycar.

Attempts to develop other sources of supply have not been very successful. Brazil is the obvious example which springs to mind. It is the home of rubber, moreover it supplies the best quality rubber in the

world. But this rubber is all wild. There are 2½ million square miles of rubber-growing area in the Amazon basin, mainly inaccessible. Attempts to develop plantations in Brazil have not been successful. The Ford Company has worked a concession on more than a million acres, but in spite of systematic efforts, including the provision of every conceivable amenity, has not been able to achieve any notable success. It is difficult to foresee any considerable expansion in the output from Brazil. During the last few years there has been considerable economic encouragement for such expansion, but no comparable results have been forthcoming.

Thus exports of rubber from Brazil to the U.S. were only 12,000 tons in 1943. With all the encouragement and pressure applied the amount available in 1944 was 30,000 tons.

African sources of supply produce only limited amounts of satisfactory material; but the quantities of all these secondary producers is ludicrously small in relation to the demands. Firestone have developed successful plantations in Liberia. There are a number of plantations under British control in Nigeria; otherwise African sources of supply are wild.

The Americans have always felt unhappy about a position which has offered them no sense of security. From a political point of view it has always been essential for their welfare that the Far Eastern plantations should be in the hands of friendly nations. With this position in jeopardy during the last few years, it is not surprising that the realistic appreciation of these disadvantages has stimulated their interest in synthetic rubber.

Cultivation of Other Rubbers. Actually about 500 plants are known which give rubber latex. These rang from milk weed with 1 per cent. to tropical *Hevea* containing about 35 per cent. There have been efforts to develop the production of the less satisfactory types of rubber in areas contiguous to the United States. For example, guayule is being extensively cultivated in Mexico, but the quantities which are likely to be available in the near future are not very considerable, while the quality of the rubber is far inferior to ordinary commercial rubber.

According to McCullum,[16] guayule is a native of North Mexico, and is a heavy woody shrub, which has supplied about 5,000 tons of dry rubber per year for many years. The rubber is not obtained in the form of latex by tapping as in the case of *hevea* rubber, but is found in the living cells, other than the leaves. The best varieties have 22 per cent. of the weight of the plant as rubber. In the past the greatest Mexican output was 10,000 tons in 1912.

There is a scheme in the United States for growing guayule in the

southern part of the country. Plants five or six years old weigh about 1 lb. and contain about 16 per cent. of rubber. The crop has to be harvested and the material deresinated. These schemes are in abeyance.

The U.S.S.R. are cultivating a type of dandelion known as *tau-sagyz* on large tracts of land in Turkestan. These give a rubber which is adequate for many purposes. The yield is said to be between 30 to 150 lbs. per acre.[17]

Another type known as *kok-sagyz* is grown on the largest possible scale. In 1942 there were 625,000 acres under cultivation. Processing developments had further increased yields. Thus whereas previously the entire plant was crushed to recover the rubber, latterly the yield has been doubled by cutting the tap root from time to time, allowing latex to flow and collecting it.[19]

Variation of Natural Rubber. One of the great difficulties rubber manufacturers have had to contend against has been the variation in the quality of rubber. For one thing, in common with all natural products rubber is never obtained pure. There are always impurities present which vary in amount according to the source of the rubber. This variation is encountered in rubber obtained from one plantation to another. It has caused a great deal of difficulty to the manufacturer and the consumer. It is extremely difficult to achieve uniformity in the case of a product such as rubber where marked differences arise according to the age and condition of trees, agricultural variations, climatic variations, etc.

In spite of the enormous amount of money at the disposal of rubber growers, only comparatively recently has a really adequately financed scheme for fundamental research on rubber been organized. According to Wilson,[31] the British Rubber Producers Research Association now spends about £40,000 a year on fundamental research. This policy of fundamental research is already beginning to show substantial results. The scientific and technical papers published by this group in recent years have been outstanding.

Without this fundamental research a thorough knowledge of their own material was thus denied to rubber growers. It is a fact that nearly all the great technical developments associated with rubber has emerged from the consumers and not from the growers. Rubber owes its eminence and importance almost entirely to the efforts of the tyre manufacturers (notably in the U.S.A.) whose technical developments have been amazing.

Little is known fundamentally about rubber, and in this respect natural rubber interests are no better off than those concerned with

synthetic rubber. Theoretically, the latter are perhaps more favourably placed since, working from pure materials, they should produce a material of definite properties and characteristics. Synthetic rubbers can virtually be made to specification. But synthetic rubbers are not yet immune from variation. This still remains an unfulfilled hope. The various products produced in the United States under Government auspices should be virtually identical. They still vary to some extent, depending upon the source of manufacture. There is also some variation as between successive batches. Many manufacturing difficulties have arisen from the variations. They have led to many involved schemes of blending and stockpiling.

These fundamental rubber problems are extremely difficult, but there has never been any attempt to tackle them on a proper scale. For example, the author contends that the oil resistance of rubber could be made satisfactory, provided that really large-scale fundamental research were attempted. If this had been attempted and achieved, it would have removed the chief technical *raison d'être* of synthetic rubber. Such a scheme necessitated employing the best technicians in the world, involving the expenditure of considerable sums. Instead of this, the same technicians have been allowed to concentrate their efforts on the development of synthetic rubber. Geer[11] posed the problem some years ago: "The rubber industry is at the cross roads with two courses before it, either to keep on along the present lines or to branch out upon a broad intensive programme of fundamental research. This idea is really but a change from the practical to the fundamental." Rubber producers took the practical path as being the route more likely to give rapid returns. It has never been properly appreciated that it is not rubber that is wanted but the properties of rubber. This attitude has been rectified in recent years.

Economic Nationalism. The causes already mentioned have contributed in part to the growth of the production of synthetic rubber. Of course, the greatest stimulus, the chief accelerating influence, has been a purely artificial one, namely the growth of economic nationalism. The grim determination of some nations to make themselves completely independent of outside sources of supply has been the powerful driving force in its production. In this respect the lead came from Germany and Russia. The Germans remembered their experiences in the 1914–18 war when lack of rubber imposed an almost unbearable strain on their war machine.

The monopolistic position with regard to supplies of raw rubber naturally encouraged such action on the part of fiercely national countries experiencing commercial difficulties. They have considered a high

price within the country to be of little importance by comparison with expenditure of foreign currency for natural rubber. The development of large-scale synthetic rubber industries in these countries has been extremely costly, but they have had their compensations. For example, although the cost of the plants has been extremely high, as also was the cost of production, yet the labour concerned in such production has been productive, and has not been allowed to stand idle. Apart from this, over a period of years large-scale production inevitably results in a lowering of costs. There is also the unpredictable influence of unexpected discoveries and new developments, tending always to bring the cost down. During critical periods such as the present, those opportunities arise which enable the millstone of the early heavy capital cost to be wiped off very cheaply.

Before the war the trend had reached Poland, Czechoslovakia, Italy and even Japan. All were interested in the possibility of producing synthetic rubber. In Japan, for example, the output in 1938 was 100 tons, and a scheme was being considered to start production of Buna in Manchuria.[5] There is little evidence of any activity in these countries at present. The vast scale of United States production makes it unlikely that any of them will persevere in this field.

So far as the countries with large synthetic industries were concerned, the pressure of war finally supplied the emphatic necessity of getting these into as large-scale production as possible.

Russia has led the way in large-scale synthetic rubber production, having been the only country which has maintained continuous research work on the subject, even from before the 1914–18 war. The same Prof. Lebedev who first polymerized butadiene in 1910 was still leading technical development and organization until quite recently. In fact the U.S.S.R. is still the only country which publishes a technical journal dealing exclusively with synthetic rubber. The Russians have also been conducting large-scale long-term experiments in the growth of rubber-bearing plants.

The Russian Government started activity in two directions:[4]

(1) To investigate the possibility of obtaining butadiene from a mixture of ethyl alcohol and acetaldehyde, according to the method suggested by Ostromislensky in 1915, for which purpose a pilot plant was erected in Moscow at the Bogatyr Rubber Company.

(2) To continue work started in 1915 by B. V. Buizov in the laboratory of the Leningrad Treugolnik Rubber Plant, using petroleum products as a source of butadiene.

A pilot factory (Experimental Station S.K.-B.) was completed in 1930, and the first batch of synthetic rubber was produced in January

1931. By the middle of that year the construction of three plants, each of an ultimate capacity of 10,000 tons of synthetic rubber per year was under way. Completed in record time, the first plant (S.K.1), located in Jaroslawl, began operations in July 1932, and was followed in September by a second one (S.K.2), in Voronezh. By 1933 two more plants were in operation (S.K.3 in Ephremov and S.K.4 in Kazan).

In 1934, 11,000 tons, and in 1935 more than 20,000 tons of sodium-butadiene polymer were produced. The second "five-year plan" called for an annual production of 90,000 tons by the end of 1937.

In 1926 Lebedev won a competition instituted to develop synthetic rubber. Basically, the process comprises the following three stages:

1. Ethyl alcohol is subjected to simultaneous catalytic dehydration and dehydrogenation, resulting in the formation of butadiene.

$$2CH_3CH_2OH \rightarrow CH_2{:}CHCH{:}CH_2 + 2H_2O + H_2$$

2. The butadiene is isolated and purified.
3. The butadiene is polymerized with metallic sodium according to the method of Matthews and Strange.

Lebedev claimed a butadiene yield of 20 per cent., based on the ethyl alcohol consumed. (The theoretical maximum is 58·7 per cent.)

In 1933 it was estimated that a synthetic rubber plant, operating at its full capacity of 10,000 tons a year, would have an hourly requirement of 3,000 kw.-hrs. of electric power, 70 tons of steam, and 1,800 cubic meters of cooling water; and would produce *inter alia* an hourly 2,000,000 calories of refrigeration and 7,000,000 calories of heat. Substantial economies have been effected since that date. Thus, to produce a ton of synthetic rubber only one-fifth of the electric power was required in 1937–38, compared to 1934, one-quarter of the steam, one-half of the heat calories, one-tenth of the calories of refrigeration, and one-third of the cooling water. Each such factory could supply 3,000–3,500 tons of acetaldehyde, 1,500–2,000 tons of ethyl ether, and some 2,500–3,000 tons of higher alcohols each year as by-products.[22]

While comparatively little is known in detail about the scale of production yet it is considerable. Nor is there much information about the location of their plants.

The first announcements of large-scale production in 1933 were met with derision. Yet in 1939, the U.S. Bureau of Commerce [2] stated that U.S.S.R. production was 50,000 tons, German production was 20,000, while United States production was 3,000 tons. No further official

information has since become available. The Russians make many types of synthetic rubber. One large establishment is known to be at Yaroslav. Sovprene is made at Erevan in Trans-Caucasia. The following table shows the production of synthetic rubber in relation to their imports of raw rubber. In view of the indisputable evidence of enormous industrial projects adequate to support a vast military machine, it is clear that synthetic rubber production must be on a great scale.

TABLE 12. U.S.S.R. FIGURES [30]

Year	Crude	Synthetic Rubber
1933	30,000	2,204
1934	47,000	11,139
1935	37,600	25,581
1936	31,000	44,200
1937	30,400	25,000
1938	26,219	53,000

German Progress. The following account explains the development of the German synthetic rubber industry. Serious research was resumed in 1925 by the I.G. Farbenindustrie ; it was greatly intensified in 1933. As the result of this work in the following year the production of Buna was announced for the first time. By the latter part of 1936 the Bayer pilot plant of the I.G. at Leverkusen was producing 80 tons per

TABLE 13. GERMAN SYNTHETIC RUBBER PRODUCTION
(*In metric tons*)

	1937	1938	1939	1940	1941	1942	1943	1944
Buna-S types—								
Schkopau	2,110	3,994	20,173	34,899	40,705	57,313	67,703	45,113
Hüls	—	—	—	2,045	25,020	36,680	34,693	39,105
Ludwigshafen	—	—	—	—	—	—	7,181	11,955
Leverkusen	Not	known	403	193	164	173	922	1,320
Total Buna S	2,110	3,994	20,576	37,137	65,889	94,166	110,499	97,493
Buna-N types—								
Leverkusen	400	640	1,126	1,898	2,631	2,824	3,656	3,129
Hüls	—	—	—	—	—	—	—	43
Total Buna N	400	640	1,126	1,898	2,631	2,824	3,656	3,172
Numbered Bunas	637	848	649	1,431	1,955	2,721	3,388	2,590
Grand total	3,147	5,482	22,351	40,466	70,475	99,711	117,543	103,255

month. In line with this activity the Continental Gummifabrike at Hanover was manufacturing 200 tyres per day and 25 per cent. of their mechanical goods from synthetic rubber. Also in 1937 it was announced that large-scale production of Thiokol had commenced at Saaru. In 1937 the plans were announced for the first really large-scale production unit at Schkopau, which was to produce 25,000 tons per year. The finance was secured by imposing a heavy import duty on raw rubber, calculated to bring in 25 million pounds, adequate to finance any synthetic rubber schemes.

In May, 1939, the Schkopau plant began production, to be followed a year later by a second similar plant at Hüls in Westphalia.

The ultimate objective was said to be 6,000 tons per month, which would make Germany independent of external sources of rubber. It was estimated that production in 1934 was 10 tons, in 1935 less than 100 tons, in 1936 1,500 tons. The target figure of 70,000 tons was reached in 1941 and maintained up to the end of the war.

It is of great interest to consider some of the important factors considered by the Germans. Here is an extract from a description of the Schkopau works by Ambros.[1]

The Schkopau Buna Works is one of the most characteristic products of the four-year plan, not only because when it was begun there was no plan or model for the large-scale production, and a completely new technique had to be developed, but also when the beginning of the building programme began in 1936, it was essential that definite production should be rapidly achieved. A great help in the development of the new works came from the fact that a pilot plant making 200 tons a month was already finished only ten months after laying the first stone, that is to say at the beginning of 1937. This small works was able to carry out valuable experiments, but it also served as a school for the training of key personnel. This is a point of extraordinary importance. In view of the complicated chemical technique it is essential to have absolutely fully trained skilled men who must be well acquainted with the technical processes, to ensure the proper handling of the apparatus and processes. The acquisition of such personnel was made possible only in this manner whereby the old I.G. Works supplied valuable personnel from their establishment near Schkopau. These key men acted as teachers in the expansion. Even so, this particular problem is not yet completely solved. The training of capable works' personnel is one of the most important features in the further expansion of the establishment.

German Production. Production was developed at four main centres which are given below, together with their planned capacities. These were, however, not all realized, partly due to difficulties in securing the necessary plant as the war progressed, but largely due to strategic bombing by the Allies. Peak output was achieved in 1943 and the third column of figures show that even the production planned

for 1944 fell considerably below the plant capacities other than for Schkopau. The actual total output for 1944 was only of the order of 100,000 tons. In 1946 German production was 15,600 tons.

Details of the four main plants are as follows:

	Capacity output (tons)	Production achieved in 1943 (tons)	Output estimated for 1944 (tons)
Schkopau	60,000	67,703	72,000
Hüls	48,000	34,293	21,000
Ludwigshafen	30,000	7,177	24,000
Auschwitz	36,000	—	24,000
	174,600	109,173	141,000

Schkopau represented the largest production unit in the scheme. Construction was started in 1937 and the plant began to produce in 1939. The plant required 15,000 employees for full production.

Hüls represented the most modern design of plant which actually came into operation. It was started in 1938 and began to produce in 1940. Hüls and Ludwigshafen were designed to be on capacity output by the end of 1943.

Auschwitz was a dispersal plant. Only part of the acetaldehyde plant came into operation and no Buna S had been produced up to the time that the plant was occupied by the Russians.

In addition to the above a plant designed for polymerization from butadiene supplied from Hüls was in existence at Leverkusen. This had a capacity of from 3,000 to 6,000 tons per year.

A plant with a capacity of 1,000–1,500 tons per year was also planned for Ferrara (Italy), but apparently never developed.

Hüls was the only synthetic rubber plant in Germany in which were made all four types of Buna S used on a commercial scale, i.e. Buna S, Buna S3, Buna SR, and Buna SS. Ludwigshafen and Schkopau produced Buna S and S3 only. All types of Buna S, including the numbered Bunas (Buna 85 and Buna 32), and the special types such as SSE and SSGF, were produced at Leverkusen which was also the chief centre for producing the acrylonitrile copolymers. Because of the danger of having this concentrated in one plant a small production of Buna N was started at Hüls towards the end of 1944, although the acrylonitrile for this was obtained from Leverkusen.

In 1943 the Germans changed from Buna S to Buna S3. The change involved slight variations of procedure using Nekal and Diproxid in the polymerization. Buna S3 was easier to process and gave superior products.

The Germans were using besides vulcanizable synthetic rubbers like Buna S, Perbunan, neoprene, Perduren and Thiokol, a number of non-vulcanizable thermoplastic products such as the polyisobutylenes, polyvinyl chlorides and methacrylic acid polymers.

United States Production. However, all these activities have been dwarfed by the immensity and tempo of the American work. Until the virtual disappearance of sources of natural rubber United States production had been on a small scale, merely keeping in step with commercial demands. It subsequently became evident that advances were considerably retarded by patent complications. Nevertheless large-scale pilot plants had been functioning successfully for several years on many types of material. In 1940 the four major rubber companies and the Standard Oil Development Co. were already producing or developing special purpose synthetic rubbers.

TABLE 14. AMERICAN PRODUCTION OF SYNTHETIC RUBBER IN RECENT YEARS (in long tons) [3]

	Total in tons
1939	2,250
1940	3,260
1941	8,400
1942	22,400
1943	231,700
1944	773,700
1945	831,000
1946	748,000
1947	509,000

The great American scheme for the production of synthetic rubber dealt with a prospective output of 1,100,000 tons per annum, the capital expenditure involved being estimated at over 200 million pounds. Of this production about 70 per cent. was to be of the Buna types based on butadiene. Buna S was adopted as the standard type. It was originally thought that the butadiene necessary for this scheme could be produced as a by-product in the 100-octane petrol plants under construction at the time.

Production of butadiene from petroleum makes use of certain highly volatile fractions of that basic material which are similar to fractions used in making high-octane aviation fuel. Consequently, the new equipment required for expanding production of these fractions was built in conjunction with existing petroleum refineries. The equipment for converting these fractions into butadiene was also erected at or near the refineries. In general, petroleum-refining companies are operating these in Texas and Louisiana, but there are three in California and a few in other states.

Materials produced to Government Specifications were known as:

GR-S which is Buna S
GR-P which is Thiokol
GR-M which is Neoprene
GR-I which is Butyl rubber

Buna-N types were made entirely by private concerns.

It is interesting to consider synthetic rubber activities in the United States in rather closer detail.

At the time of the debacle in the Far East, Du Pont de Nemours were producing large quantities of neoprene from acetylene.

There was almost complete ignorance about the chemicals involved in making synthetic rubbers. In the main they were laboratory curiosities. The technical data was meagre and unreliable.

With this background we can begin to appreciate the magnitude of the problem with which American chemists and chemical engineers have been confronted in meeting the butadiene requirements of the synthetic rubber programme. Even under the most favourable conditions there were these inherent technical difficulties in rushing such a gigantic chemical undertaking to completion. The problem was further complicated by wartime restrictions on strategic materials needed for plant construction and on raw materials.

Buna rubbers were being produced by the Standard Oil Development Company of New Jersey, by the Firestone Rubber Company, by the Hydrocarbon Chemical Corporation, and by the Goodyear Rubber Company. Thiokol was being produced by the Dow Chemical Company.

In the original programme for 1942 it was expected that 19,200 tons of neoprene and 18,000 tons of polyvinyl chloride would be made. In addition the U.S. government had authorized four plants to be run by Hydrocarbon Chemicals, Goodyear, United States Rubber Co., and Firestone from which 60,000 tons were expected. Hydrocarbon Chemicals had a private plant with 7,000 tons capacity, while Standard Oil of New Jersey were to make 10,000 tons of Buna rubber and 5,000 tons of butyl rubber.

In 1939 the only producer of butadiene was the Dow Company. In 1940 plants had been erected by the Shell Corporation, by Phillips Oil Company, by the Standard Oil Company, and by Carbide and Carbon Corporation. In 1941 Carbide and Carbon had built another plant, as had the Standard Oil Company of Louisiana, and the Shell Oil Company. The Monsanto Chemical Corporation had established equipment to produce auxiliary rubber chemicals, as had the United States Rubber Company, and the American Cyanamide Company.

TABLE 15. RATED CAPACITY OF GOVERNMENT-OWNED SYNTHETIC-RUBBER PLANTS CONSTRUCTED IN THE UNITED STATES AND CANADA, SEPTEMBER 1944

Product	Rated capacity		
	United States	Canada	Total
	Long tons		
Buna S	705,000	30,000	735,000
Butyl	68,000	7,000	75,000
Neoprene	60,000	—	60,000
Total	833,000	37,000	870,000
	Short tons		
Butadiene :			
From alcohol	220,000	—	220,000
From petroleum	406,000	30,000	436,000
	626,000	30,000	656,000
Styrene	187,500	10,000	197,500

Source : Rubber Reserve Co.

TABLE 16. BUTADIENE AND STYRENE: UNITED STATES PRODUCTION AND SALES

Year	Production	Sales		Unit value
	Quantity	Quantity	Value	
	Short tons	Short tons		Per lb.
Butadiene				
1938	0·8	0·8	$1,656	$1·09
1939	3·7	3·7	2,621	0·35
1940	184·6	138·3	98,363	0·36
1941	2,947·6	2,666·5	1,113,157	0·21
1942	12,067·2	11,990·7	4,622,246	0·19
1943	182,150·4	176,547·5	125,541,001	0·36
1947	624,000	—		—
Styrene				
1941	2,279·6	984·8	505,675	0·26
1942	4,837·4	4,798·3	2,241,054	0·23
1943	48,827·4	46,790·8	16,064,354	0·17
1945	181,000	—	—	—
1946	203,[illegible]	—	—	—
1947	[illegible]	—	—	—

Source : Compiled from [illegible]rts r[illegible]ved by the U.S. Tariff Commission from operating companies.

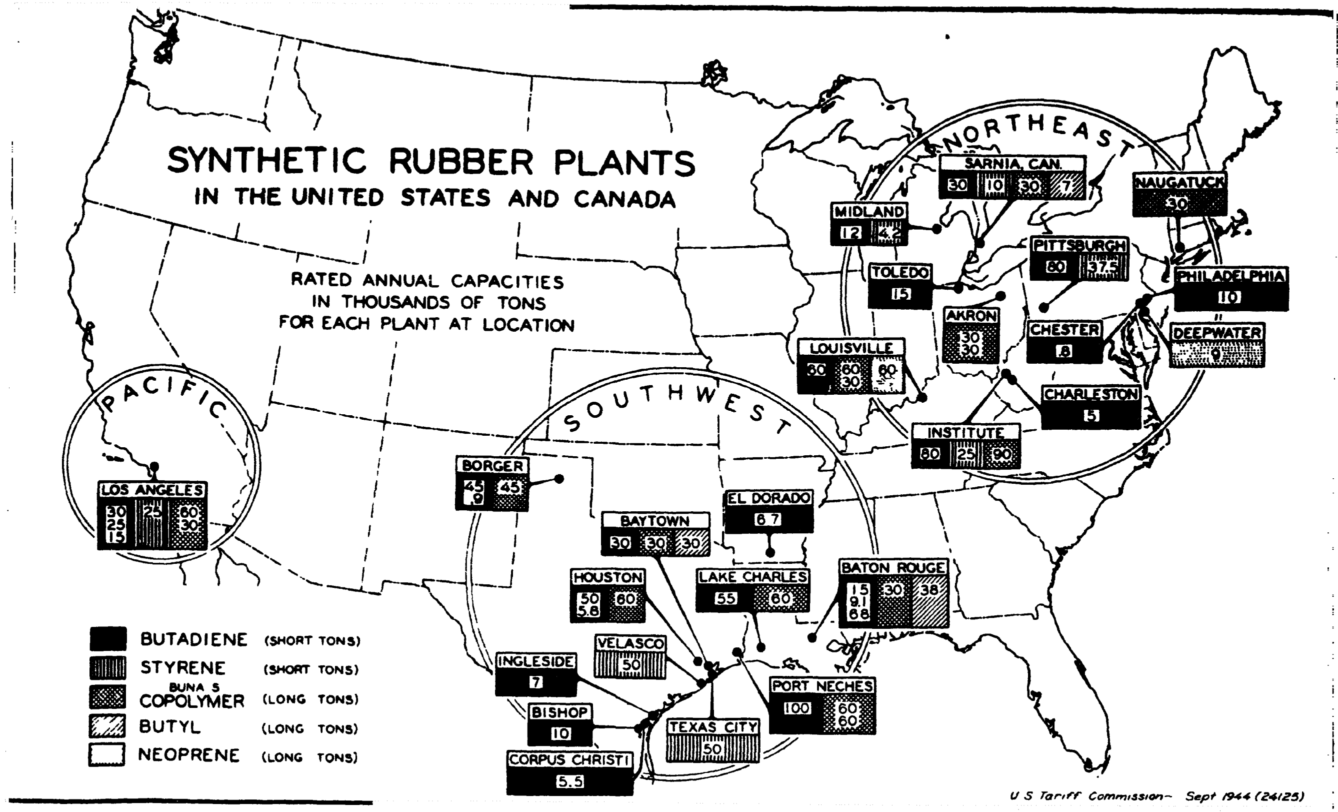


FIG. 1.—Location of Synthetic Rubber Plants.

The various rubber-like plastics were being produced by Du Pont Monsanto, Dow, Carbide and Carbon, Goodrich, Tennessee-Eastman, etc.

As a matter of fact it is interesting to note that until the situation became critical there had been considerable rivalry between petroleum interests, chemical interests, and rubber manufacturers, for leadership in these activities. This had been made quite clear in the reports of the Truman Committee. As has been pointed out, the interest of American rubber manufacturers was one of sheer self-preservation. The extremely progressive chemical concerns, with their growing interest in synthetic resin production, could not help a lively interest in the development of the closely related synthetic rubbers. The gigantic oil concerns realized the possibilities of utilizing enormous quantities of materials which for years had been thrown away, and have taken a leading part in promoting production.

The trend then set in for co-ordination of effort and rationalization. This was essential in order to achieve the greatly expanded production programme. One excellent early example was the co-operation between Goodrich Rubber and the Phillips Oil Company, who jointly own the Hydrocarbon Chemical Corporation which produces Hycar.

It is very important to note the financial weight which these concerns could bring to bear on the problem ; and it is a matter of considerable interest to study the enormous sums which have been expended on research and development work towards producing synthetic rubbers.

However by the middle of 1942 the position was chaotic with many diverse interests pulling in different directions. Drastic measures were taken. President Roosevelt appointed the Baruch Committee to lay down a definite fixed programme. The Committee was made up of Messrs. Baruch, Conant and Compton.

The position was then defined in the report of the Baruch Committee. This report estimated that the supply of rubber available to the United States in 1944 would be :

TABLE 17. PROGRAMME OF THE BARUCH COMMITTEE

	Tons
Natural rubber	68,000
Buna S	705,000
Neoprene	59,000
Butyl	132,000
Thiokol	60,000

with a recommendation for a further 140,000 tons of Buna S.

No less than 400,000 tons of Buna S was designed to come from grain at that time.

During the war production of butadiene for the synthetic rubber programme was distributed by the types of processes used as follows:

Alcohol	230,000
Petroleum base	381,700
Refinery conversions, etc.	76,800
Total	688,500 tons per year

This meant that about one-third of the butadiene was derived from alcohol and the remaining two-thirds from petroleum. How the programme was carried through may best be realized from Table 18.

TABLE 18. BUNA S COPOLYMER PLANTS IN THE UNITED STATES

Type of plant	Company owning or operating plant	Location	Rated annual capacity
			Long tons
Buna S:			
Total			706,200
Government	Copolymer Corporation	Baton Rouge, La.	30,000
	Firestone Tire and Rubber Co.	Port Neches, Tex.	60,000
	Firestone Tire and Rubber Co.	Akron, Ohio	30,000
	Firestone Tire and Rubber Co.	Lake Charles, La.	60,000
	General Tire and Rubber Co.	Baytown, Tex.	30,000
	B. F. Goodrich Co.	Louisville, Ky.[a]	60,000
	B. F. Goodrich Co.	Borger, Tex.	45,000
	B. F. Goodrich Co.	Port Neches, Tex.	60,000
	Goodyear Tire and Rubber Co.	Akron, Ohio	30,000
	Goodyear Tire and Rubber Co.	Houston, Tex.	60,000
	Goodyear Tire and Rubber Co.	Los Angeles, Calif.	60,000
	National Synthetic Rubber Corporation	Louisville, Ky.	30,000
	U.S. Rubber Co.	Los Angeles, Calif.	30,000
	U.S. Rubber Co.	Naugatuck, Conn.	30,000
	U.S. Rubber Co.	Institute, W. Va.	90,000
			705,000
Private[b]	Dewy and Almy Chemical Co.	Cambridge, Mass.	1,200

[a] One unit of this plant has been adapted to the production of 22,500 tons of Buna S or 12,000 to 15,000 tons of Buna N. It will produce Buna N only when conditions warrant—such as availability of acrylonitrile, and the demand or need for Buna N in excess of that for Buna S.

[b] Several small private plants are not listed.

Source: Prepared by the U.S. Tariff Commission from data supplied by the Rubber Reserve Company.

Of course the entire scheme has been under direct Government control, and the financial aspect has been likewise influenced by this factor. As a sidelight on this it is interesting to note the comment of the Baruch Committee:

Lest the influence of governmental policy serve to discourage the beneficial rivalries of the best brains of industry, we believe, that on the one hand there should be complete interchange of information, and on the other, as much competition in research, development and operation as possible.

The realization of these hopes has been fulfilled to an incredible degree.

TABLE 19. BUTYL, NEOPRENE, THIOKOL, AND BUNA-N PLANTS IN THE UNITED STATES

Type of plant	Company owning or operating plant	Location	Rated annual capacity
			Long tons
	Butyl plants		
Butyl:			
Total (all Government)	. . . .	. . . .	68,000
	Humble Oil and Refining Co.	Baytown, Tex.	30,000
	Standard Oil of Louisiana	Baton Rouge, La.	38,000
	Neoprene plants		
Neoprene:			
Total	. . . .	. . . .	69,000
Government	E. I. du Pont	Louisville, Ky.	60,000
Private	E. I. du Pont	Deepwater, N.J.	9,000
	Thiokol plants		
Thiokol:			
(All private)	Dow Chemical Co. (For Thiokol Corp.)	Midland, Mich.	2,900
	Buna-N plants		
Buna-N:			
Total (all private)[a]	. . . .	. . . .	20,300
	Firestone Tire and Rubber Co.	Akron, Ohio (Butaprene)	1,600
	Goodyear Tire and Rubber Co.	Akron, Ohio (Chemigum)[b]	4,200
	Hycar Chemical Co.	Akron, Ohio (Hycar OR)[b]	9,000
	Standard Oil of Louisiana	Baton Rouge, La. (Perbunan-Stanco N)[b]	5,500

[a] Several small private plants are not listed.
[b] These plants are also adapted for the production of Buna S.

Source: Prepared by the U.S. Tariff Commission from data supplied by the Rubber Reserve Company.

Table 20. Butadiene Plants in the United States

Raw material and process	Company owning or operating plant	Location of plant	Rated annual capacity
			Short tons
Alcohol:			
Total	. . .	. . .	230,000
Government	Carbide and Carbon Chemical Corp.	Institute, W.V.	80,000
	Carbide and Carbon Chemical Corp.	Louisville, Ky.	60,000
	Koppers United Co.	Pittsburgh, Pa.	80,000
Total	. . .	. . .	220,000
Private	Publicker, Inc (Bigler Chemical Co.)	Philadelphia, Pa.	10,000
Petroleum:			
Butene dehydrogenation; Total (all Government)	. . .	. . .	275,000
	Cities Service Refining Corp.	Lake Charles, La.	55,000
	Humble Oil and Refining Co.	Baytown, Tex.	30,000
	Neches Butane Prod. Co.	Port Neches, Tex.	100,000
	Shell Chemical Div. of Shell Union Oil Co.	Los Angeles, Calif.	25,000
	Sinclair Rubber, Inc.	Houston, Tex.	50,000
	Standard Oil of Louisiana	Baton Rouge, La.	15,000
Butane (all Government)	Phillips Petroleum Co.	Borger, Tex.	45,000
Naphtha, total	. . .	. . .	70,100
Government	Southern California Gas Co.	Los Angeles, Calif.	30,000
	Humble Oil and Refining Co.	Ingleside, Tex.	7,000
	Lion Oil Refining Co.	El Dorado, Ark.	6,700
	Standard Oil of Louisiana	Baton Rouge, La.	6,800
	Taylor Refining Co.	Corpus Christi, Tex.	5,500
Total	. . .	. . .	56,000
Private	Standard Oil of Louisiana (2 plants)	Baton Rouge, La.	9,100
	Carbide and Carbon Chemical Corp.	Charleston, W Va.	5,000
Total	. . .	. . .	14,100
Houdry process, total (all Government)	. . .	. . .	30,000
	Standard Oil of California	El Segundo, Calif.	15,000
	Sun Oil Co.	Toledo, Ohio	15,000
Miscellaneous petroleum methods (all private).	. . .	. . .	18,730
	Dow Chemical Co.	Midland, Mich.	1,200
	Phillips Petroleum Co.	Borger, Tex.	930
	Shell Chemical Co.	Houston, Tex.	5,800
	Ugite	Chester, Pa.	800
	Celanese Corp. (Aldol process)	Bishop, Tex.	10,000
Summary, Butadiene production—			
From alcohol:			
Government			220,000
Private			10,000
Total			230,000
From petroleum:			
Government			406,000
Private			32,830
Total			438,830
Grand total, alcohol and petroleum, Government and private			668,830

Source: Prepared by the U.S. Tariff Commission from data supplied by the Rubber Reserve Co.

TABLE 20A. U.S. SYNTHETIC RUBBER PRODUCTION

Material	Production 1946	Production 1947	Capacity 1948
GR-S	613,000	409,000	1,100,000
Neoprene	48,000	31,500	63,000
Buna N	6,000	6,600	30,000
Butyl	73,000	63,000	75,000

The estimated plant investment was more than $750 million. A total of 51 plants were designed and built.

Even Canada was to produce 46,000 tons per annum, using petroleum products supplied from the United States by pipeline.[6] In 1946 at Sarnia, Canada produced 29,000 tons GR-S and 12,000 tons GR-I.

It is a questionable point, when the Far Eastern position has been cleared up, whether it will be worth while investing the large sums that would be necessary to set up the plantation industry once again. Clearly the plantation industry could not be revived along the old anachronistic haphazard lines. It is quite certain that the enormous capital expenditure and effort involved in the American production of

TABLE 21. STYRENE PLANTS IN THE UNITED STATES

Type of plant	Company owning or operating plant	Location	Rated annual capacity
			Short tons
Styrene :			
Total . . .	. . . .	. . . .	200,000
Government	Carbide and Carbon Chemical Corp.	Institute, W. Va.	25,000
	Dow Chemical Co.	Los Angeles, Calif.	25,000
	Dow Chemical Co.	Velasco, Tex.	50,000
	Koppers United Co.	Pittsburgh, Pa.	37,500
	Monsanto Chemical Co.	Texas City, Tex.	50,000
			187,500
Private .	Dow Chemical Co.	Midland, Mich.	12,500

Source : Prepared by the U.S. Tariff Commission from data supplied by the Rubber Reserve Company.

synthetic rubber will not be allowed to be wasted because natural rubber will once again become available. This is extremely unlikely. In fact, it seems much more probable that the synthetic rubber industry will be very much cherished and preserved owing to the insurance and

freedom of action it confers upon the United States. The U.S. Rubber Act of 1948 has ensured this.

This aspect is perhaps best underlined by the extraordinary evolution of synthetic rubber latex. In 1943, latex equivalent to 300,000 lbs. dry solid content was made; this rose to 14,000,000 in the following year; in 1945 the amount was 34,000,000 lbs.; while in 1946 55,400,000 lbs. was produced. This latex activity has rounded off the rubber production programme and puts synthetic rubber on a competitive basis in all aspects.

Price of Synthetic Rubber. The question of cost is obviously an important one, and is worth some consideration. Neoprene, for example, started off in 1931 with an initial production of 250 lbs. per month, selling at $1 per lb. As the consumption and output has increased, so the price has dropped. Prices of synthetic rubbers in the United States in August 1941 were as follows:

TABLE 22. PRICES OF SYNTHETIC RUBBERS, ETC., IN 1941

	Cents per lb.
Rubber	23
Neoprene GN	65
Buna S	60
Perbunan	70
Thiokol F	45
Vistanex	45
Hycar OR	70
Koroseal	60
Polyvinyl chloride	40
Polyvinylidene chloride	58
Ethyl cellulose	50
Butadiene	20
Styrene	30
Acrylic nitrile	36

At this time all were at comparatively low rates of production hardly greater than pilot plant quantities. Naturally the price picture has altered as production has got into its stride. During the war Rubber Reserve Co. received the following prices:

	Cents per lb.
Natural rubber	$22\frac{1}{2}$
GR-S	$18\frac{1}{2}$
GR-I	$15\frac{1}{2}$
GR-M	$27\frac{1}{2}$

plus $17\frac{1}{2}$ per cent. per lb. surcharge for "War Orders".

Cramer [8] has given an interesting study of the prices to which the various materials must drop in order to be competitive with natural rubber. These figures have been brought up to date.

TABLE 23. COMPARATIVE ECONOMIC PRICES

Product	Aug. 1941 price	Density	Equivalent price	1947 price
Natural rubber . . .	$0.23	0·92	0.23	0·2575
Neoprene GN (GR-M) .	0.65	1·24	0.17	0·275
GR-S	0.60	0·96	0.22	0·185
Perbunan	0.70	0·96	0.22	0·40
Thiokol F	0.45	1·38	0.15	0·45
Vistanex	0.45	0·90	0.24	0·32
Koroseal (30 per cent. plasticizer) . . .	0.60 (est.)	1·33	0.16	0·36
Hycar OR . . .	0.70	1·00	0.23	0·47
GR-I		0·92	0·23	0·185

Farish [10] prophesied in early 1942:

Buna rubber at first will cost 30 c. a pound when made from butadiene derived from petroleum. When plants are running at maximum efficiency the cost will be reduced to 20 c. a pound or less. The first Butyl rubber will cost about 20 c. a pound but the price may eventually be reduced to between 10 c. and 15 c. a pound. Buna rubber plants at first originally estimated to cost $1000 a ton of annual capacity, are now figured to cost about $600. Butyl plants, first estimated to cost as high as $750 a ton are now expected to cost about $350 a ton of annual capacity.

The price of Government Buna-S rubber had been set at 50 cents per lb. in 1942. In 1943 the price was cut sharply to 36 cents per lb.

Collyer [7] has said that average cost of all GR-S made up to the beginning of 1945 was approximately 32 cents per lb. In some factories it had been made at 14 cents per lb. exclusive of amortization and depreciation of plant.

German prices are of some interest. In 1944 Buna S and Buna S3 cost 1 Reichsmark per lb., Plastikator 32 was 1·1 Rm. per lb., Perbunan was 1·5 Rm. per lb. and Koresin was 1 Rm. per lb. These were selling prices. Costs of production were between one-half and two-thirds of these values.

Post-War Cost of Synthetic Rubber. Recently there have been several authoritative statements regarding the cost of synthetic rubbers. The situation is continually changing, but the ultimate price picture does begin to emerge.

Gilliland and Lavender [13] have gathered together much of pertinent data relative to rated capacities, total production to date, ultimate capacity, estimated investment cost by plant, source of funds, and other information.

They showed that the seventeen Government-owned butadiene plants have a rated capacity of 626,000 tons per year, represent a total investment of $346,633,296, and that investment cost per annual ton

of estimated actual ultimate capacity will be \$398·00. The five Government-owned styrene plants have a rated capacity of 188,500 tons per year, represent a total investment of \$82,750,000, and investment cost per annual ton of estimated actual ultimate capacity will be \$285·00. Investment per annual ton of estimated actual ultimate capacity for GR-S is set at \$663·00, for Neoprene GN at \$717·00, and for Butyl at \$779·00. The average cost of all synthetic rubbers in the Government programme is estimated to represent an investment of \$675·00 per long ton on the basis of estimated actual capacity, or slightly more than 30 cents per lb.

Operating costs, current in June 1944, excluding feedstocks, amortization, preliminary expense and research, are listed as 2·21 cents per lb. for butadiene from alcohol and 4·63 from butylene (dehydrogenation), 2·52 cents for styrene, and 4·83 cents for the copolymer. Post-war costs are estimated at 2·19 and 4·48 cents for butadiene, 2·51 cents for styrene, and 4·44 cents for the copolymer. Current operating costs, including feedstocks but excluding amortization, preliminary expense and research, are shown at 24·04 cents per lb. for Neoprene GN and 21·51 cents for Butyl. Post-war operating cost for Neoprene GN is estimated at 19·58 cents per lb.

According to Gilliland and Lavender, GR-S could be produced at an out-of-pocket cost of 12·2 cents per lb., with styrene and butadiene at 7 and 8 cents per lb., respectively. In 1948, according to Hadlock,[14] out-of-pocket cost of GR-S was 14 to 14·5 cents per lb. while the price to cover all charges, etc., was 18·5 cents. The Canadian selling price was 16–16½ cents per lb.

Future of Butyl Rubber. In 1939 the Standard Oil Development Company [23] investigated the possibilities of butyl rubber in relation to crude rubber. They analysed the possible applications of butyl

TABLE 24. POSSIBLE OUTLETS FOR BUTYL (AS AT OCTOBER 1939)

Uses (based on 1937–38 figures)	(a) lbs. per year	(b) lbs. per year
Cable insulation	13,000,000	—
Miscellaneous tubing	10,000,000	13,000,000
Tank car lining	(no data)	—
Packing, washers, gaskets	5,000,000	5,000,000
Inner tubes	—	100,000,000
Tyre curing bags	8,000,000	—
Coated fabric	5,000,000	5,000,000
Mechanical goods	50,000,000	50,000,000
Flooring	1,000,000	1,000,000
Sponge	—	10,000,000
Druggists' sundries	5,000,000	5,000,000
Total	97,000,000	189,000,000

rubber (*a*) in fields where they believed butyl rubber to have a definite advantage, and (*b*) where they expected or hoped that it would have an advantage. At this time they estimated in each instance that butyl rubber would be available at between 30 to 40 cents per lb. as compared with natural rubber at 15 to 20 cents per lb. The table on page 50 gives the result of their investigation.

At that time they were not sufficiently optimistic as to be certain that inner tubes would fall in the (*a*) group. As they pointed out even 10 per cent. of the inner tube business would amount to 10 million pounds per year.

Although butyl rubber—GR-I—has not yet reached the production level initially specified, yet the progress is such as leaves no doubt about its potential importance.

It is clear that they were very conservative, since the most recent estimate, on the large scale costs butyl rubber at 6·6 cents per lb. while rubber stands at 22½ cents. Even a year later than when the above estimate was made, the possible field for butyl rubber, apart from tyres, was estimated at 250,000 tons per annum.

Actually GR-I was plagued with numerous production difficulties. Actual production in the U.S.A. was 23 tons in 1942; 1373 tons in 1943; 20,252 tons in 1944; 1945 it was 52,378 tons; in 1946 it was 80,823 tons; and in 1947 it was 62,824.

Consumer Position at Present Time. Much of the improvement in performance has been due to the development of new compounding ingredients, notably soft furnace blacks. Many mechanical goods in the United States are considered to give better performance when based on GR-S in place of natural rubber, and the same is true of cable insulation.

Since the middle of 1943 the United States has been virtually on a synthetic rubber basis. There has been ample quantitative evidence to vouch for the performance. From that time until the end of 1946 there have been produced approximately:

Passenger car tyres	100,000,000
Truck tyres .	60,000,000
Farm tyres . .	10,000,000
Inner tubes .	170,000,000
Synthetic retreads	90,000,000

In view of the remarkably short transition period the performance of these tyres exceeded all expectations. The somewhat poor performances experienced in the early days have been improved beyond recognition. Passenger tyres gave mileages about 10 per cent. less than corresponding natural rubber tyres. There was a slight falling

off in fuel efficiency and acceleration. Truck tyres gave about 25 per cent. less life, chiefly owing to heat build-up and ply separation. GR-S tubes were not very satisfactory and there was an almost complete changeover to GR-I.

The officially approved types of tyres in the United States involve the following compositions :

S.4.	GR-S 87 per cent., Natural rubber 13 per cent.	Agricultural tyres.
S.7.	GR-S 33 per cent., Natural rubber 67 per cent.	Large car tyres; small truck tyres.
S.9.	GR-S 67 per cent., Natural rubber 3 per cent.	Large car tyres.
S.11.	GR-S 6 per cent., Natural rubber 94 per cent.	Truck tyres, aircraft tyres.

American Interest in Growing Rubber. The Standard Oil Development Company has studied every aspect of the synthetic rubber production and usage. These included comprehensive market surveys. In one such survey in 1940[24] they considered the leading producers of tyres in the United States which consume a very large proportion of the total world production of rubber. The main objective was to show the salient facts of the tyre industry, those facts that would be of importance in evaluating the rôle a competitive synthetic rubber might play.

One interesting angle was the financial interest of the large American Rubber Companies in growing their own rubber. They showed that Goodyear, United States Rubber, and Firestone, owned rubber plantations large enough to yield 20–25 per cent. of their needs, as shown in the accompanying table. The Goodrich Company has never gone in for rubber growing.

TABLE 25. VALUE OF RUBBER PLANTATIONS (ESTIMATED) [25]

		U.S rubber (dollars)	Goodyear (dollars)	Firestone (dollars)
A	Planted area . .	19,800,000	11,650,000	12,800,000
	Unplanted . .	150,000	210,000	1,000,000
	Book value	19,950,000	11,860,000	13,800,000

ACREAGE

B	Acres owned .	132,000	100,723	1,000,000
	Acres planted	99,000	58,125	(1936) 64,000
	Acres tapped	57,350	51,752	(1936) 16,000

To develop and use these plantations to their fullest extent, according to the survey, additional expenditures amounting to \$200–\$400 per acre, for a 5–7 year period when trees mature, would be necessary. At the lower cost the following expansion and additional expense would be involved:

TABLE 26. COST OF DEVELOPING PLANTATIONS

	Additional rubber per year (lbs.)	Total production percentage of own demand	New investment (dollars)
U.S. Rubber	13,000,000	31	6,500,000
Goodyear	17,000,000	28	8,400,000
Firestone	21,000,000	30 [a]	13,000,000

[a] 30% production is taken for Firestone to be on a comparable basis with the other two.

Considering the out-of-pocket cost of growing rubber as 6 cents per lb., and adding other out-of-pocket charges, the following showed that these companies would be forced to stop growing rubber if the price in New York dropped permanently to about 8½ cents per lb.

	Cents per lb.
Cost of rubber at plantation (out-of-pocket)	6·0
Cost of container at 45 cents at 10 per ton (2,240 lbs.)	0·20
Ocean freight at \$15.00–\$18.00 per ton (2,240 lbs.)	0·67
All ocean risk at 22½ cents per \$100	0·04
Talc and labour for packing / Labour for handling / Exchange, export tax } Assumed	1·5
Out-of-pocket cost, New York	8·41

Cost at the point of consumption would be increased by freight and handling charges. Freight to Akron (the chief rubber manufacturing centre) is 0·43 cents per lb.

Financial statements of the U.S. Rubber plantations prior to absorption by the parent company in 1938 allowed the price picture to be developed from another angle, as shown in Table 27 on page 54.

The price of rubber at New York may be then broken down to:

	Cents per lb.	%	%
Out-of-pocket cost	8·4	79	55
Other costs	2·3	21	15
Total cost, New York	10·7	100	
Earnings	4·7	—	30
Average price, New York	15·4	—	100

TABLE 27. FINANCIAL STATEMENT OF UNITED STATES RUBBER COMPANY PLANTATIONS

Year	Produced pounds (millions)	Earnings Dollars (millions)	Earnings cents per lb.	Rubber price New York (cents)	Total cost of rubber (cents)
1934	50,986	1,735	3·4	12·9	9·5
1935	42,054	967	2·3	12·4	10·1
1936	42·185	1,913	4·6	16·4	11·8
1937	58,072	4,589	7·8	19·4	11·6
Average	48,324	2,301	4·7	15·4	10·7

According to the Standard Oil Survey this earnings figure is probably somewhat higher than is actually the return to most growers, as brokerage and trading expenses must be deducted. Companies like U.S. Rubber, Goodyear, and Firestone should not be concerned with general trading expenses on their own production. The original investment on the U.S. Rubber Company's plantations was about $38,000,000, and the book value to-day is about half this sum. The productive life of the rubber tree is not known; some trees are still producing at seventy years. But taking forty years as the life and with a production of 50 million pounds per year, the investment amounts to 1·9 cents per lb. or 83 per cent. of the " Other costs " item (2·3 cents). On a basis of producing 50 million pounds per year the earning would be:

TABLE 28. PLANTATION EARNINGS

Rubber price, New York (cents)	Earnings per year (dollars)	Return on investment (%)	Book value (%)
12	650,000	1·7	3·4
15	2,150,000	5·6	11·2
20	4,650,000	12·2	24·4

which checks previous information that 12 cents was a living price for the plantations. These data actually show 10·7 cents to be the breaking-point for profits. The main conclusion is of great interest. *Rubber permanently between* 8 *and* 11 *cents per lb., New York, should warrant shutting down the plantations if a satisfactory, abundant substitute were to become available.*

Cost of Equipping Plantations.—Trainer and Babcock, of the Firestone Tyre & Rubber Co.,[27] have given some interesting estimates of costs of natural rubber. In 1940 they estimated that rubber produced in a modern plantation could be delivered to New York at between 7 and 8 cents per lb. This figure would represent production costs and shipping costs. This was based on the assumption that the capital investment of the plantation was being written off on a 20–25 year basis. They estimated that a plantation of 100,000 acres would cost about 40 million dollars completely equipped, and would produce about 25,000 long tons of natural rubber per year.

The Standard Oil Development Company, in considering the production of butyl rubber, examined these estimates. They concluded that the production of 100 tons of butyl rubber per day involved an investment of about 10 million dollars with production cost of 7·5 cents per lb. They estimated that the investment cost for the same quantity of rubber would be something over 50 million dollars, i.e. five times the investment required for an equal amount of butyl rubber. They deduced from this that if butyl rubber could be made as suitable as natural rubber for tyres, the manufacture of the material on a large scale would be economically sound. For the production of GR-S on a corresponding scale they estimated a capital cost of something like 21 million dollars and a production cost of about 16 cents per lb.

It is as well to bear in mind that some rubber plantations will have to start from scratch once again. The above analysis gives an indication of the scale of finance likely to be involved.

Until quite recently there has been a great deal of scepticism in this country as to the likelihood of realizing the low costs of synthetic rubbers which have been suggested.

The pundits must remember their own oft-repeated predictions as to the impossibility of large-scale production. So far as price is concerned they have proved notoriously unreliable in forecasting the price of their own commodity. None forecast the possibility of rubber dropping from 6*s*. per lb. in 1925 to 1½*d*. per lb. in 1931; nor that during the depression the price of reclaimed rubber would be considerably higher than that of the raw material. It is therefore most unwise to be pontifical or dogmatic about the prospects of synthetic rubber. This is especially the case in view of the fact that American technicians have only just been permitted, or encouraged, to bring their full weight to bear on the problem, a state of affairs which is almost certain to produce astonishing results when it comes to fruition. As Stine, Vice-President of du Pont de Nemours, said: ". . . under the pressure

of a great war there may be compressed scientific, economic and social developments that might have taken many decades to achieve under less urgent conditions." [26]

To bring the matter into perspective it is just as well to point out that eighteen years ago there was no synthetic rubber on offer; thirteen years ago synthetic rubber was at 5*s.* per lb., with a negligible production. Eight years ago production was of the order of 30,000 or 40,000 tons a year. To-day production is probably of the order of 800,000 tons per annum.

Collyer puts the subject into something like true perspective: ". . . Natural rubber took 70 years to move from 4,000 tons per year to 781,000 tons in 1941—production in the use of synthetic rubber has covered in the main greater range than that in a mere 5 years, moving from 1,750 tons in 1939 to around 800,000 tons in 1944 . . ."

It was only late in 1942 that the first bulk delivery of synthetic rubber—now referred to as GR-S—arrived in Great Britain. No sooner had we settled down properly to its wide-scale application than natural rubber reappeared.

Synthetic Rubber Reclaim. Large amounts of ordinary reclaim have been used in synthetic rubber manufacture. The reclaiming of all current types of synthetic rubber has been successfully carried out. The great difficulty at the present time is the segregation of different types of synthetic rubber. With the large-scale use of synthetic rubber, commercial methods for reclaiming them have become very necessary. For natural reclaim must in due course come into short supply. And reclaimed rubber of one type or another is essential to large-scale manufacture of rubber products. At the present time the volume of reclaimed synthetic rubber is relatively small. Neoprene reclaim has been available for some years.

The use of synthetic rubber has a great influence on accessory materials. The poorer heat behaviour favours the use of rayon

TABLE 29. PRODUCTION, CONSUMPTION, EXPORTS AND STOCKS OF RECLAIM

(*In long tons*)

	Production	Consumption	Exports
1941	274,202	251,231	13,851
1942	295,114	254,820	30,405
1943	303,991	291,082	15,678
1944	260,607	251,083	11,800
1945	243,309	241,036	13,413
1946	295,612	275,410	14,461

instead of cotton, for carcases. Even nylon is being used. It also involves the consumption of ever-mounting quantities of special type of carbon black. So much so that at the present time there is a serious shortage. Some indication of the position may be obtained from Table 29 opposite.

TABLE 30. CARBON BLACK

Production, Shipment and Stocks—U.S.A. (*in thousands of pounds*)

	Production	Shipments Domestic	Export	Total	Approximate producers' stocks (end of period)
1941	594,065	496,579	148,165	644,744	118,847
1942	574,006	334,296	115,635	449,931	242,755
1943	593,427	524,388	104,912	629,300	205,215
1944	801,860	780,439	156,991	937,430	69,243
1945	1,052,798	846,262	173,773	1,020,035	102,005
1946	1,227,272	N.A.	N.A.	1,199,013	130,260
1947	1,318,474	—	—	—	—

N.A. – Not available.
Sources: Bureau of Mines, 1941 5; Selected Trade Circles, 1946.

REFERENCES

[1] AMBROS, *Kunststoffe*, 1939, **29**, 106.
[2] BARKER, *Rubber History, Production and Manufacture*, U.S. Department of Commerce, 1940.
[3] BLAKE, *India Rubber World*, 1945, III, 577.
[4] BORISOVITCH, *Kauchuk i Rezina*, 1939, **10**, 5.
[5] BRIDGEWATER, *Ind. Eng. Chem.*, 1941, **33**, 1342.
[6] Bulletin R. G. A., 1934, **16**, 793.
[7] COLLYER, *India Rubber World*, 1945, III, 560.
[8] CRAMER, *Ind. Eng. Chem.*, 1942, **34**, 24.
[9] CRANE, *India Rubber World*, 1942, **107**, 260.
[10] FARISH, *India Rubber World*, 1942, **106**, 476.
[11] GEER, *Ind. Eng. Chem.*, 1935, **27**, 362.
[12] General Rubber Co., *Fortune*, 1936, **14**, 146.
[13] GILLILAND and LAVENDER, *Chem. Eng. News*, 1945, **23**, 193.
[14] HADLOCK, *India Rubber World*, 1948, **117**, 513.
[15] HOLT, *India Rubber World*, 1940, **101**, 43.
[16] MCCULLUM, *India Rubber World*, 1941, **103**, 33.
[17] PINCUS, *Rubber Age* (N.Y.), 1941, **40**, 179.
[18] *Rubber Age* (N.Y.), 1942, **50**, 310.
[19] *Rubber Age* (London), 1943, **24**, 256
[20] *Rubber Statistical Bulletin*, 1947, **1**, 7.
[21] Rubber Stocks, *India Rubber World*, 1941, **104**, 1335.

[22] *Sintet Kauchuk*, 1935, **3**, 4
[23] Standard Oil Co , *India Rubber World*, 1941, **103**, 287
[24] —— *U S Committee on Patents*, Part 6, p 2975 Washington, 1942
[25] —— *U S Committee on Patents*, Part 6, p 3041 Washington, 1942
[26] STINE, *India Rubber World*, 1942, **107**, 50
[27] TRAINER and BABCOCK, *U S Committee on Patents*, Part 6, p 3050 Washington, 1942
[28] U S Plants, *India Rubber World*, 1942, **106**, 595
[29] —— Programme, *Chemical and Metallurgical Engineering*, 1942, **49**, 89
—— Tariff Commission Report on Rubber—Washington, Sept 1944, p 85.
[30] U S S R , *India Rubber World*, 1940, **101**, 63
[31] WILSON, Private Communication

PART II

CHEMICAL AND PHYSICAL BACKGROUND OF SYNTHETIC ELASTIC MATERIALS

CHAPTER 3

TERMINOLOGY

Synthetic Rubber Terminology. The number of materials having rubber-like properties increases at a steady rate. Many of these materials have no relation with one another, and certainly not with natural rubber; yet they are all referred to as "synthetic rubber", which has become something of an omnibus term.

For some time there has been growing confusion in rubber terminology. The arrival of numerous synthetic rubber-like materials has made matters considerably worse. It is very desirable to give close study to the definition of synthetic rubber.

The Approach of Rubber and Plastics.[1] It has been apparent for a long time that the gap between rubber and plastics has been filling in rapidly. The author has made a special point of stressing this during recent years.[2] Synthetic rubbers now fill the space. The result is that there is no very clear demarcation between rubber and synthetic rubbers on the one hand, nor between synthetic rubber and plastics on the other.[3] Thus Perbunan resembles rubber very closely in many respects, while no one has been bold enough to state categorically whether polyvinyl chloride is a synthetic rubber or a thermoplastic (although most opinion tends towards the latter). Yet again, what is polyisobutylene to be classified as? It is more rubbery than rubber yet is thermoplastic and cannot be vulcanized.

One important point is the matter of perspective. Since these new materials are no longer solely in the province of rubber technology, any system of nomenclature must be founded on lines which are much wider than apply for rubber alone. It is a grave error for rubber technologists to endeavour to impose their own extremely involved and unsatisfactory terminology on the new field. It is all very well to apply new expressions, for example, for the polyvinyl family of resins as if they were quite new, when all the time there exists a perfectly good and widely used name—"ethenoid" resins proposed by Redfarn. The same reasoning applies to "thioplasts" which is a very satisfactory term for the polysulphide type of material.

For one thing all sorts of accessory materials are now employed which are novel in rubber technique, such as plasticizers, e.g. dibutyl phthalate, tricresyl phosphate, etc. They are, however, commonplace in the plastics industry, and in the lacquer industry.

The issue is not only a scientific one, but is complicated by commercial considerations which cannot be lightly set aside. At the present time anything having rubbery properties is immediately hailed as a synthetic rubber. It is impossible to take a completely detached view of the matter. It must be recognized that descriptions such as "synthetic rubber" always have strong public appeal. and it will require strong and persistent efforts to introduce any new terms.

Rubber is an Unsatisfactory Term. To start with, the very name "rubber" is a most unfortunate term. It is difficult to understand how the mere fact that it could erase marks from paper could have developed into a generic term for the material. It should also be noted that rubber is not an international term, which is a grave disadvantage.

Rubber is the keyword of the industry, but as Dawson [7] has stated:

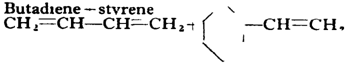
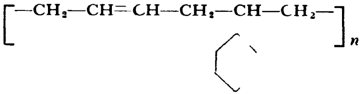
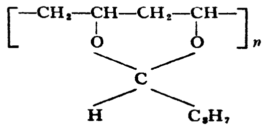
> It is commonly used without qualification to connote such diverse ideas as highly derived caoutchouc, raw or crude rubber of many botanical species, soft vulcanized rubbers in endless variety, hard rubbers, synthetic rubbers, and so-called synthetic rubbers. One has but to think of such common phrases as the empirical formula of rubber, sheet rubber, rubber-soled shoes, oil-resisting rubber, to appreciate how much is taken for granted every day.

In this connection the rubber industry cannot logically complain at the term "synthetic rubber", for no efforts have been made to alter equally inaccurate designations such as "reclaimed" rubber.

Many of the troubles of rubber terminology arises from the fact that insufficient fundamental research has been carried out on rubber, and too little is known about it, and here it is perhaps appropriate to emphasize again that most work has been done not by scientists of countries interested in growing rubber, i.e. not by producers, but by consumers of rubber. Thus, while rubber is invariably a material having high molecular weight, which present methods are inadequate to define, there is as yet no real scientific basis for comparison between any two rubbers or between rubber and a synthetic material. The situation is further complicated by the fact that up to the present rubber has never been synthesized. None of the many materials based on isoprene has ever achieved this distinction. No commercial material can pretend literally to be synthetic rubber, for they all differ completely chemically from rubber. In any event rubber is itself a variable material.

Numerous Rubber-like Materials. The position at present is that there are numerous materials possessing rubber-like properties. Many are capable of undergoing a thermal change from the plastic to the elastic condition. In some cases this is promoted by the use of

TABLE 31. STRUCTURAL RELATIONS AMONG MONOMERS AND POLYMERS

Monomers	Basic recurring groups of polymers	Nature of product
Isoprene $CH_2{=}\overset{\displaystyle CH_3}{\overset{\vert}{C}}{-}CH{=}CH_2$	$\left[-CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{C}}{=}CH-CH_2-\right]_n$	Natural rubber
Butadiene $CH_2{=}CH-CH{=}CH_2$	$\left[-CH_2-CH{=}CH-CH_2-\right]_n$	Buna 85 and 115 (German) SKA and SKB
Butadiene + styrene 		Buna S, Buna SS
Butadiene + acrylonitrile $CH_2{=}CH-CH{=}CH_2 + CH_2{=}\underset{\displaystyle CN}{\underset{\vert}{C}H}$	$\left[-CH_2-CH{=}CH-CH_2-\underset{\displaystyle CN}{\underset{\vert}{C}H}-CH_2-\right]_n$	Buna N, Perbunan, Hycar OR*, Chemigum*
Butadiene + isobutylene $CH_2{=}CH-CH{=}CH_2 + \overset{\displaystyle CH_3}{C}{=}CH_2$, $\underset{\displaystyle CH_3}{}$	$\left[-CH_2-CH{=}CH-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-CH_2-\right]_n$	Butyl rubber*
Chloroprene $CH_2{=}\overset{\displaystyle Cl}{\overset{\vert}{C}}-CH{=}CH$	$\left[-CH_2-\overset{\displaystyle Cl}{\overset{\vert}{C}}{=}CH-CH_2-\right]_n$	Neoprene
Vinyl chloride $CH_2{=}\underset{\displaystyle Cl}{CH}$	$\left[-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{C}H}-\right]_n$	Koroseal, Flamenol, Vinylite Q
Isobutylene $\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}{=}CH_2$	$\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-CH_2-\right]_n$	Vistanex
Dichloroethyl ether + sodium tetrasulphide $ClCH_2-CH_2-O-CH_2-CH_2Cl + Na_2S_4$	$\left[-CH_2-CH_2-O-CH_2-CH_2-\underset{\displaystyle S}{\underset{\Vert}{S}}-\underset{\displaystyle S}{\underset{\Vert}{S}}-\right]_n$	Thiokol B
P V A. + butyraldehyde $\left[-CH_2-\underset{\displaystyle OH}{\underset{\vert}{C}H}-CH_2-\underset{\displaystyle OH}{\underset{\vert}{C}H}-\right]_u + C_3H_7CHO$		Butacite, Butvar, Vinylite X

* Identity not disclosed by the manufacturer but reported to be of the type indicated

sulphur. In other instances materials other than sulphur are able to promote the change. Other rubber-like materials do not undergo the change, but remain permanently thermoplastic.

As regards the term " synthetic rubber ", Dawson has stated " The controversy centres around the choice between two interpretations:

(*a*) that a synthetic rubber should be identical with or at least closely related to natural rubber in a chemical state,

(*b*) that a synthetic rubber should reproduce the outstanding physical characteristics of rubber."

The first definition would limit the use of synthetic rubber to butadiene rubbers. The second term includes all materials that are rubbery. This second interpretation is the more widely accepted.

Yet these materials by virtue of possessing only some of the more evident rubbery properties are referred to as synthetic rubbers. Where can the line be drawn?

A number of leading authorities have considered the question very closely. Definition of rubber has been a highly controversial subject. There is now a definite trend to get away from the use of the word " rubber " for substances other than where common usage applies. This trend is particularly marked for synthetic materials.

Definitions of Synthetic Rubber. Houwink [10] has supplied a very controversial definition of a rubber-like material; " an organic material may be called a rubber when it shows a high elasticity of 100 per cent. or more at room temperature, and when it does not lose this property upon storage at room temperature during considerable periods." Yet this definition is hopelessly out of date, since many butadiene materials show little elastic behaviour at ordinary temperatures. Stevens [19] criticized this definition very strongly chiefly on the grounds that materials other than natural rubber come within its scope.

A more satisfactory general definition was given by Midgley [15] who considered the matter along these lines,

it is impossible at the present time to define synthetic rubber in chemical terms . . . expressed in physical terms the simplest definition is—" those substances which possess the physical properties of rubber ". Such a statement is functional, and should be revised in terms defining a unique physical property of rubber. Many organic substances of high molecular weight may be stretched to many times their original lengths, examples being gums, tars, waxes, jellies, and so on, but only rubber forcibly retracts to substantially its original size and shape after stretching, so that the definition becomes " synthetic rubbers are those organic substances which possess the property of forcibly retracting to approximately their original size and shape after being greatly distorted, i.e. such as being stretched x per cent of their original length ". Here x is some arbitrary value. It should be over 100, probably 400, possibly 600, but certainly not higher.

This definition has the merits of including almost every type that has so far been put forward.

Wood [22] takes "synthetic rubber" to mean merely a synthetic substance which has physical properties resembling those of natural rubber, that is it can be stretched a considerable amount, e.g. 300 per cent., and when released will quickly and forcibly retract to substantially its original dimensions.

Bridgewater [5] described "synthetic substances with rubber-like properties" as substances that resemble rubber in the simple property of extensibility or deformability under moderate loads coupled with a tendency to recover their original form when the load is removed, although not necessarily to a degree comparable to the recovery exhibited by natural rubber.

Schade [18] has summarized the position in a very realistic fashion:

> The meaning of the word rubber has changed. It no longer signifies a particular hydrocarbon material but has been widely adopted to characterize a class of substances similar physically to natural rubber regardless of their chemical composition; in order to qualify as a rubber a material should stretch readily to a considerable degree and after release retract forcefully and quickly; but no specific criteria have been generally accepted limiting the values for these properties.

Trumbell and Sloan [21] suggested that the term "synthetic rubber" should be restricted to the polymers obtained from monomeric organic substances containing conjugated double or triple bonds or copolymers involving these materials. According to Fisher, it would be best to reserve the term "synthetic rubber" for products that are chemically related to natural rubber, that is to the various derivatives of butadiene.

It is desirable to have some single term to cover all rubber-like products. Among suggestions that have been put forward as generic terms for this type of material are "Collastics" by Barron,[4] "Lastics" by Ellis,[8] "Elastoplasts" by Stevens,[19] while Naunton [16] suggested "Elastoplastics", and Patterson [17] has put forward the suggestion of "Cauchoid". While all these have been favourably commented upon, the one which has received most general acceptance to date was actually suggested by Fisher.[9] He suggested the use of the term "Elastomer", and this has come into fairly wide usage. Moore [14] has put forward a companion term "Plastomer" to cover the non-elastic plastic substances, "Elastomer" being considered as referring to the elastic or rubber-like substances.

Terminology Suggested by Fisher. Fisher [9] extended his efforts in terminology to devising general terms for the more or less sharply defined groupings of materials which have rubber-like properties.

ELASTOMERS	ELASTOPRENES (DERIVATIVES OF BUTADIENE)	Butadiene rubbers : Sodium butadiene rubber, Russia. Buna rubbers, Germany. Piperylene rubbers.
		Isoprene rubbers : Polyprene : natural rubber. Sodium isoprene rubber. Heat-polymerized isoprene rubber.
		Dimethylbutadiene rubbers : Cold polymer : methyl rubber H. Heat polymer : methyl rubber W.
		Haloprene rubbers : Polychloroprene rubber : neoprene. Polybromoprene rubber.
	ELASTOLENES	Polymers, such as polyisobutylene, formed in the presence of a catalyst-e.g. boron trifluoride : Vistanex, Oppanol B.
	ELASTOTHIOMERS	Polyalkylene sulphides: Thiokol, Perduren.
	ELASTOPLASTICS	Rubber-like polymers of acrylic and methacrylic esters : Acronal, Plexigum. Rubber-like mixed glyptals. Plasticized polyvinyl chloride : Koroseal, Igelite, Mipolam. Polyvinyl acetate, above 40° C. Polystyrene, above 65 C., and when partially solvated. Polyarylenethylenes or polyxylenes : AXF, from benzene, ethylene chloride, and aluminium chloride. Polyphosphonitrilic chloride $(PNCl_2)x$, an inorganic rubber.
PLASTOMERS	TRUE THERMOPLASTICS	Shellac, polystyrene, polyvinyl acetate, celluloid, cellulose acetate.
	THERMOSETTING PLASTICS	Bakelite, glyptals, formaldehyde-urea polymers, acrylic resins.

For example, he suggested " Elastoprenes " to apply to the rubber-like polymers of butadiene and its derivatives, including chloroprene. He suggested " Elastolene " for materials similar to polyisobutylene. For the polyethylene sulphide type such as Thiokol, he suggested " Elastothiomers ", and for the growing class of rubber-like plastics which include polyvinyl chloride, methyl methacrylates, and the glyptals, he suggested using the term " Elastoplastics ". He pointed out that while many of the materials were not of a rubber-like nature,

yet it was well worth bringing them under consideration in order to avoid inappropriate terminology.

Other systems have been put forward, for example Jacobs [11] devised four groupings for synthetic rubbers. He suggested (*a*) Halo Rubbers, as applying to the neoprene type, (*b*) Co-Rubbers, referring to the butadiene type, (*c*) Thio-Rubbers for the Thiokol and Perbunan, and (*d*) Plasto-Rubbers or Reso-Rubbers, which were intended to apply to vinyl polymers, and their unvulcanizable thermo-plastic polymers made from hydrocarbons.

Another scheme was that formulated by Kindscher.[12] He divided all rubber-like materials into three groups ; crude rubbers were referred to as Kautschukgene ; the second grouping, the synthetic rubbers from butadiene, etc., Thiokol, neoprene, and so on, being classified as Kautschukoide ; the third group, the rubber-like polyvinyl derivatives, polyisobutylene, and so on, being referred to as Gummoide.

In discussing this question of rubber terminology, Trumbell and Sloan submitted the classification of synthetic polymeric substances based upon the chemical composition as follows :

TABLE 33. SYNTHETIC POLYMERIC SUBSTANCES

I. Inorganic.
II. Organic.
- A. Saturated polymers with only carbon atoms in the chain.
  - (*a*) Hydrocarbons.
  - (*b*) Substituted hydrocarbons :
    1. Containing halogen (made from vinyl halide).
    2. Containing acid, ester, or nitrile groups.
    3. Co-polymers of (1) and (2).
- B. Unsaturated polymers with only carbon atoms in the chain.
  - (*a*) Hydrocarbons (polymers of butadiene and its homologues, and of monomers containing more than one point of unsaturation.)
  - (*b*) Co-polymers involving butadiene and its homologues.
  - (*c*) Halogen containing polymers of butadiene and its homologues.
  - (*d*) Alkoxy or Aryloxy-containing polymers of butadiene and its homologues.
  - (*e*) Acid, ester, or nitrile derivatives of butadiene and its homologues.
  - (*f*) Thioplastics.
- C. Polymers in which oxygen, nitrogen, and perhaps sulphur, as well as carbon, enter into the formation of the chain
  - (*a*) Polymeric amides.
  - (*b*) Polymeric esters.
    1. Aliphatic acid esters.
    2. Alkyd resins.
- D. Derivatives of cellulose.
- E. Derivatives of urea.
- F. Reaction products of phenolic substances with aldehydes.

G. Derivatives of natural rubber.
  (*a*) Thermoprenes.
  (*b*) Reaction products obtained by the action of stannic chloride, aluminium chloride, etc.
  (*c*) Reaction products with halogen acids.
  (*d*) Reaction products with halogens.

As has already been pointed out this merely emphasizes the fact that there is no clear demarcation between rubber and plastics. In some of the instances quoted by Trumbell and Sloan, rubber-like properties of plasticity and elasticity are evident in the raw materials and are merely emphasized by the incorporation of plasticizers. In other instances these properties may be latent and will only become apparent after addition of suitable plasticizers. It is in these cases that plasticizers are referred to as " elasticizers ".

Highly polymerized rubber-like materials have been divided by Stöcklin [20] into two general classes; (1) synthetics capable of vulcanization—(*a*) butadiene copolymers and (*b*) reaction products of dihalogenated aliphatic compounds with sodium polysulphide ; (2) synthetics incapable of vulcanization—(*a*) polymerized isobutylenes (similar to Vistanex) and polymerized acrylic acid esters (similar to Plexigum and like materials) and (*b*) products having rubber-like properties in combination with certain plasticizing agents (for example, Koroseal).

Cramer [6] has outlined a scheme for defining these rubbery materials more closely. His scheme is as follows:

TABLE 34. DEFINITIONS OF SYNTHETIC RUBBERS

1. True synthetic rubbers, or elastoprenes, derived from butadienes, or these constituted homologues unsaturated :
   A. Simple butadiene polymers.
   B. Modified butadiene polymers.
      1. Butadiene plus styrene, as typified by Buna S.
      2. Butadiene plus acrylic nitrile, as typified by Perbunan.
   C. Substituted butadiene polymers.
      1. Polymers of isoprene.
      2. Polymers of methyl isoprene.
      3. Polymers of chloroprene, as typified by neoprene.
   D. Modified butylene polymers.
      1. Butylenes plus small amounts of butadiene or other diolefines, as typified by butyl rubber.
2. Synthetic rubber-like elastics or elasto-plastics saturated :
   A. Polyalkanes.
      1. Polybutylene as typified by Vistanex.
      2. Polyphenylene-ethylene as typified by A.X.F.
   B. Polyvinyl derivatives.
      1. Polyvinyl alcohol.
      2. Polyvinyl chloride-acetate copolymer, as typified by Vinylite.
      3. Polyvinyl chloride as typified by Koroseal, Vinylite Q, and Flamenol.
      4. Vinylidene chloride, as typified by Saran.

5. Polyvinyl acetals, such as Formvar; butyral, as typified by Butvar, Vinylite X, and Butacite.

C. Reaction products of aliphatic halides plus alkali polysulphides.
1. Ethylene dichloride, plus sodium tetrasulphide, as typified by Thiokol A.
2. Dichlorethyl ether, plus sodium tetrasulphide, as typified by Thiokol B.

D. Miscellaneous elasto-plastics.
1. Plasticized polyacrylic esters as typified by the Acryloids.
2. Alkyd condensation products as typified by Duraflex.
3. Cellulose derivatives such as ethyl cellulose.

In his recent book Marchionna [13] has gone to great trouble to evolve a comprehensive system of nomenclature. His ideas have received some measure of approval in the United States.

TABLE 35

Group abbreviations adopted are as follows:

I. *Butalastics-1* includes the polymers from monomeric diene hydrocarbon compounds having conjugate double bonds, and no substituents on the carbon atoms other than hydrocarbon radicals (e.g. the German Bunas 85 and 113; sodium butadiene, the "methyl" rubbers, etc.).

II. *Butalastics-2* covers polymers of one type of butadiene compound with a different type of butadiene compound, or butadiene compounds in varying degrees of polymerization (e.g. a polymer of butadiene with natural rubber would be included).

III. *Butalastics-A*—interpolymers of butadiene with acrylic and methacrylic acids, and their esters or ethers.

IV. *Butalastics-B* covers interpolymers of a butadiene compound with a polymerizable benzene ring compound (e.g. styrene, and therefore covering rubbers such as Buna S).

V. *Butalastics-E*—interpolymers of a butadiene hydrocarbon with an unsaturated hydrocarbon having an ethylenic linkae, such as ethylene, butylene, and the like (e.g. "Butyl").

VI. *Butalastics-N* includes interpolymers of a butadiene hydrocarbon with any compound containing nitrogen (e.g. acrylic nitrile, and, therefore, Buna-N types and the like).

VII. *Butalastics-V* relates to interpolymers of butadiene with a vinyl compound, excluding aromatic compounds with a vinyl chain.

VIII. *Butalastics-X* covers miscellaneous co- or interpolymers of a butadiene with compounds not otherwise classified (e.g. with terpenes, oils, etc.).

IX. *Butalastics-H1* covers polymers of any substituted butadiene in which the substituent is or contains a halogen (e.g. the neoprenes).

X to XVI. *Butalastics-H2*, *HA*, *HB*, *HE*, *HN*, *HV*, *HX*, all classify co- or interpolymers of a haloprene with various compounds in which the specific features are, respectively, butadiene or a haloprene, acrylic acid, a benzene ring, an unsaturated olefinic compound having one double bond, nitrogen, a vinyl compound, other not classified groups.

XVII. *Butalastics-3* groups all those polymers from three or more polymerizable substances including at least one butadiene compound.

A Simple System. Actually all this has become rather complicated. More and more synthetic resins are coming into the synthetic rubber orbit. It is suggested that a perfectly workable scheme of nomenclature can be developed out of all the suggestions so far put forward. It is submitted that the fundamental keyword, the generic term for all materials having rubber-like properties should be " elastics ". The term is in universal use as an adjective, to describe every form of rubber, so why not employ it as a name ? Everybody knows already what the word implies ; it is a familiar household term. Moreover, it is international. Using this there is therefore a very satisfactory division into the " natural elastics ", which includes ordinary rubber, and all the other secondary natural rubbers. Then there are the " synthetic elastics ", that is to say, those which are not found in nature, but have to be made chemically. These can be more closely defined in groups to some extent following the lines already suggested.

It is absolutely essential that some system of nomenclature should be decided upon immediately, and stressed by every possible means, for it must be realized that we are still only on the threshold of this field of activity. As new materials begin to pour in under the pressure of work dictated by present circumstances, an utterly chaotic situation may develop, unless something is done at an early stage to organize the terms of reference.

The nomenclature suggested here in many respects conforms to current practice which is a great advantage.

TABLE 36. ELASTICS

NATURAL ELASTICS :

1. *Rubber.*

   Hevea brasiliensis ; Ficus elastica ; Urceola elastica ; Landolphia, Funtumia ; *Manihot glaziovii,* Guayule, etc.

2. *Natural isomers of rubber.*

   Gutta-Percha ; Balata, etc.

SYNTHETIC ELASTICS :

1. *Elastomers.*

   Materials which might reasonably be called synthetic rubbers, being unsaturated materials based on butadienes, or members of the butadiene family. These are vulcanizable. These would include Buna S, Perbunan, Hycar, Chemigum, Neoprene, etc.

2. *Elastenes.*

   Materials which are based on olefines and are virtually saturated, e.g. polyisobutylene, polythene, A.X.F., and butyl rubbers.

3. *Ethenoid.*

   Materials based on the polyvinyl grouping, e.g. polyvinyl chloride, acrylic esters, etc.

4. *Thioplasts.*
   Materials based on olefine dihalides and alkali polysulphides.

5. *Elastoplasts.*
   Plastics which have a very limited phase of elastic properties, either by physical or chemical changes, e.g. polystyrene, alkyd resins, cellulose esters, etc.

In this system, every general group name is already widely used except the term " elastene " which is here suggested for the first time.

REFERENCES

[1] BARRON, " Approach of Rubber to Plastics," *Chem. and Ind.*, 1938, **57**, 159.
[2] —— " Rubber Plastics," *Brit. Plastics*, 1938, **9**, 377 et seq.
[3] - " Rubber Industry and Plastics Industry," *I.R.J.*, 1937, **97**, 89.
[4] - -- - *J. Soc. Chem. Ind.*, 1936, **55**, 844.
[5] BRIDGEWATER, *India Rubber World*, 1938, **100**, 21.
[6] CRAMER, *Ind. Eng. Chem.*, 1942, **34**, 24.
[7] DAWSON, *Proceedings of The Rubber Conference*, London, 1938, p. 1006.
[8] ELLIS, *Ind. Eng. Chem.*, 1936, **28**, 1138.
[9] FISHER, *Ind. Eng. Chem.*, 1939, **31**, 941.
[10] HOUWINK, *Elasticity, Plasticity and the Structure of Matter*, Cambridge Univ. Press, 1937, p. 223.
[11] JACOBS, *Caoutchouc and Gutta-percha*, 1938, **35**, 35.
[12] KINDSCHER, *Kautschuk*, 1938, **14**, 140.
[13] MARCHIONNA, *Butalastic Polymers – Their Preparation and Applications.* Reinhold, New York, 1946.
[14] MOORE, *Ind. Eng. Chem.*, 1939, **31**, 944.
[15] MIDGLEY, *Rubber Chem. Tech.*, 1937, **10**, 678.
[16] NAUNTON, *J. Soc. Chem. Ind.*, 1936, **55**, 297.
[17] PATTERSON, *Ind. Eng. Chem.*, 1939, **31**, 944.
[18] SCHADE, *Rubber Age* (N.Y.), 141, **48**, 387.
[19] STEVENS, *J. Soc. Chem. Ind.*, 1936, **55**, 814.
[20] STÖCKLIN, *Trans. I.R.I.*, 1939, **15**, 51.
[21] TRUMBULL and SLOAN, *India Rubber World*, 1941, **104**, 33.
[22] WOOD, *Nat. Bureau of Standards Circular 427*, 1940.

CHAPTER 4

HISTORICAL BACKGROUND OF SYNTHETIC ELASTICS

The Beginnings of Synthetic Elastics. The academic background of synthetic rubbers is similar in many respects to that of raw rubber. At first the main idea was to try to analyse rubber by breaking it down, and then to endeavour to build it up again. In spite of all attempts this has never been achieved. And, indeed, until it was realized that this approach to synthetic rubber was not a satisfactory one, production of synthetic rubber was in a complete rut, and never made much progress.

The chemistry of the rubber hydrocarbon isoprene is the basis upon which synthetic rubber chemistry is built. So it is desirable to briefly survey the work carried out on rubber, especially as in many instances it was associated with efforts to produce synthetic rubber. In fact, most of the work carried out until the last war had the dual purpose of learning about the structure of rubber, and by the use of this knowledge to synthesize rubber.

From about 1910 onwards these objectives became separated and diverged. Thereafter while rubber technologists made amazing strides in developing the physical properties of rubber compositions, the secrets of rubber structure have baffled all efforts and remain the subjects of speculation even to this day. Most chemical work was devoted towards the production of synthetic rubber-like materials.

The available information about rubber chemistry and structure, since it is in effect the behaviour of polymerized isoprene, is very pertinent to the study of synthetic rubber. Already similar chemical derivatives are being prepared from other butadiene polymers.

Action of Heat on Rubber. From quite early times rubber was subjected to heat and the products examined. Ordinarily rubber begins to soften at about 120° C., starts to decompose above 170° C., and as the temperature rises it changes into a thick brown oil with a characteristic odour, which is no longer rubbery. Above 300° C. cracking takes place, and breakdown occurs with the formation of numerous decomposition products.

Himly [13] obtained two fractions ; " faradayin ", and a high boiling fraction of " caoutchene ". Williams [44] distilled the former and isolated a pure liquid hydrocarbon boiling between 37° and 38° C., which he

called Isoprene. He found this to be empirically C_5H_8. Bouchardat [2] distilled rubber, and obtained in addition to isoprene other hydrocarbons such as dipentene and heveene. Empirical analysis showed them to be simple multiples of isoprene. Then Tilden [36] worked out the structure of isoprene which proved to be 2-methyl-1,3-butadiene.

$$CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}\ \ CH\ \ CH_2$$

It was subsequently demonstrated by Wallach [39] that dipentene could be derived from two molecules of isoprene on the basis of Thiele's [34] theory of partial valencies.

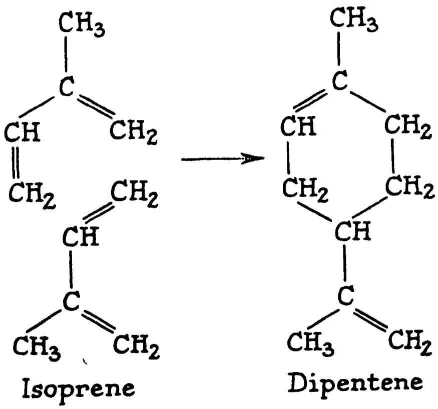


FIG. 2.

Polymerization of Isoprene. In the meantime it had been discovered that isoprene could be converted into rubber-like material. Williams discovered that on standing, isoprene tended to become viscous. Bouchardat [1] found that by heating isoprene with strong hydrogen chloride he obtained an elastic rubber-like product in a much shorter time than when the change was allowed to occur by standing. The possible industrial significance of the fact that isoprene could be polymerized was clearly noted for the first time by Tilden,[38] who wrote, " It is this character of isoprene which gives it a somewhat practical interest, for if it were possible to obtain this hydrocarbon from some other and more accessible source (than rubber) the synthetical production of India rubber could be accomplished." Tilden converted isoprene which he obtained from turpentine into a rubbery material by the action of hydrogen chloride, a conversion which was also aided

by the use of nitrosyl chloride. This change was found by Wallach in 1887 to be promoted very effectively by the use of ultra-violet light.

Isoprene monopolized all the attention in these early efforts at polymerization. In 1892 Tilden [37] reported that he had found isoprene to undergo spontaneous polymerization to caoutchouc. He stated that samples of isoprene, prepared from turpentine, which had been stored in bottles for several years, had given rise to solid masses of rubber.

> The artificial rubber [he wrote] like natural rubber, appears to consist of two substances, one of which is more soluble in carbon disulphide or benzene than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characteristics with a similar preparation from Para rubber. The artificial rubber unites with sulphur in the same way as ordinary rubber, forming a tough elastic compound.

It was only in 1900 that Kondakoff [18] discovered that dimethyl butadiene when heated with alkaline potash gave a rubber-like material.

Shortly afterwards Thiele [35] showed that piperylene, a material isomeric with isoprene, polymerized to a rubbery product when left in the dark for some time. It was then quite evident that the ability to form rubbery material was not specifically confined to isoprene, being shared at least by closely related materials. It is, therefore, strange that it was only in 1910 that Lebedev,[20] another Russian chemist found that the parent material of this group, namely butadiene, could be polymerized to produce an elastic material.

TABLE 37. BUTADIENE DERIVATIVES KNOWN AT THIS STAGE

		B.P.	Density
Butadiene . . .	CH_2 CH—CH CH_2	4° C.	—
Isoprene . . .	CH_2 C—CH—CH_2 $\quad\;$ | $\quad CH_3$	33° C.	d^{20} 0·6804
Piperylene . . .	CH_3.CH CH—CH—CH_2	42° C.	d^{20} 0·679
Dimethyl Butadiene	CH_2 C—C CH_2 $\quad\;$ | $\;$ | $\quad CH_3$ CH_3	69·5° C.	d^{20} 0·7273

Many workers showed when rubber was broken down by heat, that in addition to isoprene, many other materials were formed all isomeric with isoprene. This led to the inference that rubber was a polymer of isoprene having a composition expressed by $(C_5H_8)_x$. It was also inferred that the long-chain molecule formed broke up in

such a way as to give isoprene or polymers of isoprene. The highest recorded yield of isoprene obtained by destructive distillation of rubber has been obtained by Bassett and Williams,[3] amounting to 23 per cent.

Harries Ozone Reaction. By 1900 there was already a very lively interest in the production of synthetic elastic materials. But there was an obstinate determination to make synthetic rubber. Nothing else would do. Consequently it was necessary first to elucidate the structure of the natural material and criteria for the artificial materials. In this field the work of Harries was outstanding. The momentous study of the effect of ozone on rubber by Harries [11] is one of the classical features of rubber chemistry.

Harries showed that one molecule of ozone joined on to each double bond of an olefine to give an amorphous viscous material which was an ozonide. These were often explosive. When warmed

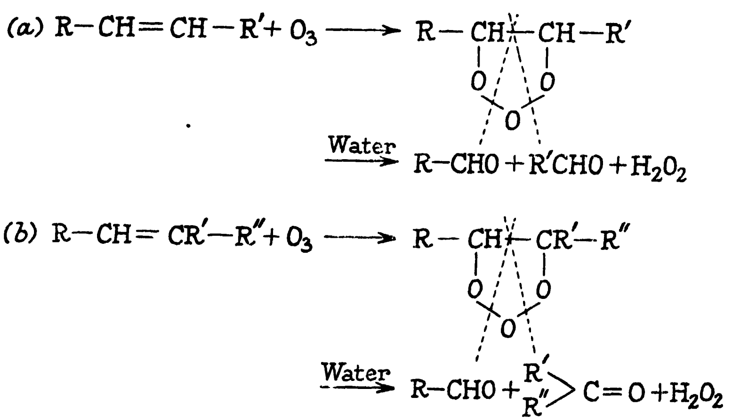


FIG. 3

with water an ozonide decomposes in a regular fashion giving aldehydes and hydrogen peroxide, or ketones and hydrogen peroxide according to whether the carbon atoms at the double bond have hydrogen or alkyl groupings attached.

Thus rubber when subjected to ozone treatment yielded substantially levulinic aldehyde and levulinic acid. These are 1 : 4-dicarbonyl compounds, as are others such as succinic dialdehyde or acetonylacetone. It is essential for the formation of such compounds that a double bond should recur after each fourth carbon atom in a carbon chain.

If the double bonds are located in a different way or are removed by cyclization, then an abnormal rubber results. Consequently if

elastomers resemble rubber then comparable decomposition products will be obtained. It is the nature of these products in many instances which has lent support to the theory that many of them are long open-chain molecules comparable with the rubber molecule.

In his efforts to work out the structure of rubber Harries produced

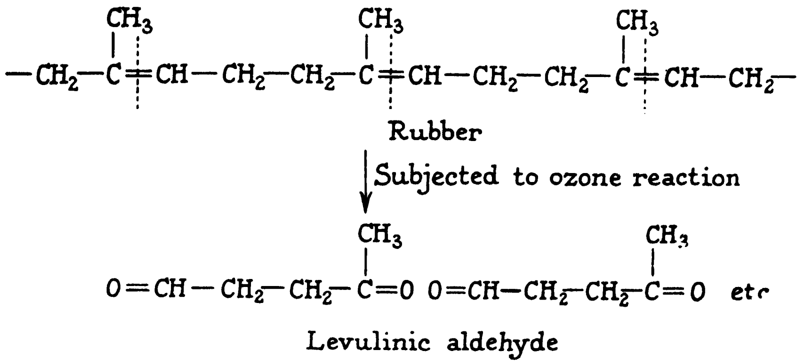


FIG. 4.

a number of materials having the same ultimate composition as rubber, but very different properties. These were the iso-rubbers, which were much less unsaturated than natural rubber.

The procedure was to convert rubber in benzene solution into rubber hydrochloride and then to remove hydrogen chloride. Although resembling rubber in some ways, it was a different material. In particular, the products he obtained after ozone treatment were different from those obtained with rubber. This meant that the double bonds were in different positions. By forming a hydrochloride with this iso-rubber, and again removing it, yet another different product was obtained which he called beta-iso-rubber. As a result of his work with ozone, Harries suggested an eight-membered ring structure for rubber.

$$\begin{array}{l} CH_3\text{—}C\text{—}CH_2\text{—}CH_2\text{—}CH \\ \qquad\;\; \| \qquad\qquad\qquad\quad \| \\ \qquad\; CH\text{—}CH_2\text{—}CH_2\text{—}\,C\,\text{—}CH_3 \end{array}$$

FIG. 5.—Harries' 8-membered ring.

Pickles [30] suggested that rubber is made up of a long chain of recurring isoprene units joined together by undergoing the Thiele transformation. By this an isoprene molecule becomes an isoprene unit,

i.e. forming a 1 : 4 conjugated system which joins up with other units to form the chain.

$$\begin{array}{l} CH_2{-}\,C{-}CH{=}CH_2 \\ \quad\;\;\; | \\ \quad\; CH_3 \end{array}$$

Isoprene molecule

$$\begin{array}{l} -CH_2{-}C \;\; CH{-}CH_2{-} \\ \qquad\;\;\; | \\ \qquad\; CH_3 \end{array}$$

Isoprene unit

$$\begin{array}{l} -CH_2{-}C \;\; CH{-}CH_2{-}CH_2{-}C \;\; CH{-}CH_2{-} \\ \qquad\;\;\; | \qquad\qquad\qquad\qquad\quad\;\; | \\ \qquad\; CH_3 \qquad\qquad\qquad\qquad CH_3 \end{array}$$

Isoprene units join together to form a chain of unknown length expressed as

$$-\left[\begin{array}{c} CH_2{-}C{-}\;CH{-}CH_2 \\ | \\ CH_3 \end{array}\right]_x-$$

FIG. 6.

This conception that rubber is made up of a long chain of recurring isoprene units, i.e. as a polymer of isoprene, is the one generally accepted at the present time. It is no longer thought necessary to explain rubber properties and polymerization by means of the presence of secondary valencies. A good case for explaining such behaviour as being due to primary valencies was made by Whitby,[41] drawing on his work not only with rubber but with butadiene and polyethylene.

The work of Staudinger[32, 33] on the formation of high molecular weight in long-chain polymers also shows that the assumption of secondary valencies as connecting links is unnecessary. Carother's[6] work also tends to confirm this.

The Second Phase. The importance of Harries' work on the structure of rubber was that it paved the way for the first efforts to make synthetic rubber on a commercial basis. As already described, he established a number of criteria to distinguish rubber. To test these he had to make a number of synthetic rubbers. He was quite familiar with the synthetic rubber position, because in 1902 he had polymerized isoprene by heating it strongly, without getting really satisfactory products. He had shown that rubber was made up of isoprene units, which simplified the problem to one of obtaining isoprene and then developing a suitable method for making the isoprene molecules link up. The work he carried out had very important

repercussions. According to Memmler:[22] "These important degradation results which made possible the actual characteristics of a rubber substitute, together with the rising price of rubber in 1909 greatly stimulated attempts to produce artificial rubber."

As events turned out, the desire for absolute precision, i.e. to make artificial rubber, retarded the successful production of synthetic material, for subsequently it became evident that the rubbery properties were the important feature, not the exact composition. It is interesting to observe how in all his writings Harries particularly refers to "artificial" rubber, not "synthetic". He, more than anyone, realized that rubber had not been synthesized.

First Commercial Interest. Harries' work was of such great interest to the Bayer Company, and the Badische Anilin Fabrik in Germany, that they were prepared to sponsor extensive work aimed at the production of synthetic rubber.

The time was propitious, for natural rubber was at a very high price, and in 1910 reached nearly 15*s.* per lb. Also at that time the plantation industry had not yet become established, and rubber was a variable unsatisfactory raw material. So that the conditions at that time were very much different from the present, and any laboratory product that could be produced possessing rubbery properties had bright commercial prospects. Nowadays such materials would in the ordinary way be quite hopeless. They must have marked superiority in some properties.

In due course, working for the Bayer Company, Hoffman and Coutelle[15] were able to polymerize isoprene by heating it at temperatures below 200° C. for about eight days in the presence of catalysts. Hoffman claimed that prior to the work in 1909 no one had ever made synthetically "the tough, elastic, nervous caoutchouc colloid". Whitby and Katz[42] do not agree with this view.

If the ground is taken that the synthesis of rubber has been achieved only when there has been made a product strictly identical with natural rubber in every particular respect, identical not only chemically but also in the degree of polymerization as indicated by the colloid and elastic properties before and after vulcanization—then, it must be declared that such synthesis has even yet to be accomplished; but, on the more reasonable ground that the production from isoprene of an elastic, vulcanizable product generally similar to natural caoutchouc constitutes a synthesis of caoutchouc, then the honour of having first made the synthesis must go to G. Bouchardat and Tilden.

Harries' earlier attempts along similar lines had failed because the temperatures that he employed were too high. Harries[10] eventually succeeded in effectively polymerizing isoprene at a much lower tem-

perature, namely 100° C., having acetic acid as catalyst and using pressure.

These discoveries inaugurated a really active era in the production of synthetic rubber. This concerted effort laid the foundations on which present-day production has been built.

Discovery of Rubber Accelerators. Arising out of this work there came many extremely important commercial developments. In fact, it cannot be stressed too much that although synthetic rubber may have only become practicable during recent years, yet numerous valuable by-products have emerged from the enormous amount of work directed towards its manufacture, and it has had profound effects on many other unrelated industries. An outstanding example of a profoundly important discovery in a closely related industry was the arrival of accelerators for rubber.

The synthetic materials which were in course of preparation were found to oxidize with great ease. Various materials were added to try to offset this tendency, some being extremely successful. But in addition to exerting a distinct retarding effect on oxidation they also increased the rate of vulcanization. The arrival of accelerators was the result, as described in the very important Bayer patent.[4]

According to Gottlob,[9] who was associated in all this work on synthetic rubber:

> There are certain kinds of synthetic rubber which decompose quickly from oxidation. These can be protected against oxidation very effectively if a small addition of organic base is mixed with them. As protective material, such bases as aniline, pyridine, quinoline, dimethyl aniline, and in certain cases piperidine were used. While the bases first mentioned in the above list produced no essential change during the vulcanization of the particular variety of rubber involved, the rubber in which 1 per cent. of piperidine was used showed a completely different behaviour after vulcanization. The determination of combined sulphur showed that about eight times as much sulphur had combined with the rubber as the accepted amount under normal conditions ; a truly astonishing result. This observation made by Hoffman and Gottlob introduced us to investigating the action of piperidine on the vulcanization of natural rubber, whereby similar results were obtained.

This supplied the basis for the first Bayer patent on accelerators.

Organic accelerators of vulcanization, now universally used in rubber manufacture and which have contributed greatly to the advance of rubber-manufacturing technique and to the improvement in the quality of rubber goods, were first discovered in the United States by Oenslager and Marks.[24] Their use was kept secret. They were discovered independently and patented in Germany by the Bayer

Company. Their discovery followed directly out of work on synthetic rubber. The use of piperidine, originally applied to synthetic rubber as an antioxidant and later found to be an accelerator of vulcanization, was followed by the use of the compound prepared by the action of piperidine on carbon disulphide, viz. piperidine pentamethylene dithiocarbamate. If the dithiocarbamate is used with natural rubber in a simple rubber-sulphur mixture, it is in fact little more efficient as an accelerator than piperidine. If, however, it is used in the presence of zinc oxide, it is much more active than piperidine, causing vulcanization to occur at least twenty-five times as quickly as does piperidine.

Since zinc oxide is such a common component of technical rubber mixtures, it was inevitable that this fact should sooner or later be found out. And with its discovery the whole field of ultra-accelerators was opened up.

In course of time accelerators and the accompanying antioxidants moved out of the synthetic rubber orbit and materially contributed towards the development of rubber manufacture.

The results of the first great burst of activity towards synthetic rubber production can briefly be summarized as they seemed in 1910. Lebedev had just discovered that butadiene could be polymerized to give a rubbery material, and it was evident that the butadiene family of materials, distinguished by containing conjugated double bonds, could be turned into rubbery materials. Heat or ultra-violet light were effective in causing the change which was promoted by the presence of catalysts and by the use of pressure. This phase was very much concerned with the problem of polymerization and emphasis was laid on the importance of double bonds. Numerous materials had been discovered which acted as catalysts. It laid the groundwork on which subsequent successful production has been based.

Developments Preceding the Last War. Production of synthetic rubber was a matter of the greatest interest during the years immediately preceding the last war. This was the period of the second distinct phase in synthetic rubber development. There were three prominent groups of chemists working on the problem, in England, in Russia, and in Germany.

In view of the fact that in recent years British activity in the synthetic rubber field has been virtually non-existent, it comes as something of a surprise to realize that British chemists were extremely prominent in synthetic rubber development, and made great contribution towards its production. Very extensive and successful research work was carried out at Manchester under W. H. Perkin, junior.[28] Associated with him in the work were Matthews, Strange, and Weiz-

mann.[29] A number of laboratory processes were developed for making the various butadiene derivatives. Their most successful method was to make aldol from acetaldehyde which they obtained from ethyl alcohol. The aldol was reduced to butylene glycol which was then

$$\underset{\text{Acetaldehyde}}{CH_3.CHO + CH_3.CHO} \longrightarrow \underset{\text{Aldol}}{CH_3.CH(OH).CH_2.CHO}$$

$$CH_3.CH(OH).CH_2.CHO \xrightarrow{\text{reduce}} \underset{\text{Butylene glycol}}{CH_3.CH(OH).CH_2.CH_2OH}$$

$$CH_3.CH(OH).CH_2.CH_2OH \xrightarrow{\text{dehydrate}} \underset{\text{Butadiene}}{CH_2\quad CH{-}CH\quad CH_2} + 2H_2O$$

FIG. 7.

catalytically dehydrated. Singularly enough, this was essentially the method which the Germans ultimately adopted in 1928, to start their large-scale production. Another of Perkins' methods was to chlorinate butylene glycol and then to treat the product with soda-lime which also yielded butadiene.

Another method was based on butyl alcohol. This was dehydrated to 1,2-butylene by passing over phosphoric acid at 450° C., converted to the dibromide, and then passed over soda-lime which removed hydrogen bromide and left butadiene. Fernbach [7] was associated with

$$\underset{\text{Secondary butyl alcohol}}{CH_3.CH(OH).CH_2.CH_3} \xrightarrow{\text{dehydrate}} \underset{\text{Butylene}}{CH_3.CH\quad CH.CH_3}$$

$$CH_3.CH\quad CH.CH_3 \xrightarrow{\text{bromine}} CH_3.CHBr.CHBr.CH_3$$

$$CH_3.CHBr.CHBr.CH_3 \xrightarrow{-2HBr} \underset{\text{Butadiene}}{CH_2\quad CH{-}CH\quad CH_2}$$

FIG. 8.

much of this work, having developed his famous process for the fermentation of starch to yield chiefly butyl alcohol. The modification of this process as worked out by Weizmann [40] to yield pure acetone was of outstanding assistance to Great Britain during the last war. Commenting on this work, Whitby and Crozier [42] have pointed out that

> although the processes which were developed in England prior to the war for the production of synthetic rubber have never established themselves commercially, the Fernbach fermentation process which was developed along with them has proved to be of great importance and may be said to represent a by-product of the programme of work on synthetic rubber which has more than justified the latter.

A good account of much of this work has been given by Schotz.[30]

Many other important by-products since that time emphasize the wisdom of this attitude.

Perhaps the greatest achievement which emerged from this source was the discovery that the polymerization of the butadienes was profoundly accelerated by the use of sodium. Matthews and Strange [21] patented this discovery in 1910. Their method was to polymerize butadiene in the gaseous state in the presence of sodium wire.

It is a remarkable feature of almost every rubber development of major importance that simultaneous discoveries appear to be made elsewhere. So it proved in this case. Harries and the Bayer Company [12] had discovered almost the identical process at almost the same time. Harries' method essentially was to put butadiene with 3 per cent. sodium wire into a sealed tube. After a comparatively short period of heating at 40° C., a solid mass was formed, which when washed with alcohol to remove sodium, gave a light yellow rubber-like material. With isoprene treated in this way for five days an almost theoretical yield was obtained. Holt [16] found that the process was greatly facilitated and better products resulted by working in the presence of carbon dioxide.

About this time in the United States, Kyriakides and Earle [19] were working along somewhat similar lines. They stated ". . . The problem will eventually be solved, although it will require a good many years of patient and earnest study. The starting-point in these syntheses will most probably be alcohol, which can be produced fairly cheaply."

As has almost become the custom in the rubber industry, long and involved litigation followed, the outcome of which was that the English chemists established in the Law Courts their priority in this discovery.

The Production of Raw Materials. It is of interest to consider briefly some of the methods utilized for the production of raw materials up to this time. This was the formative period in the production of synthetic rubbery materials. But it was also the formative time for many synthetic resins, such as polyvinyl chloride, etc. The difficulties being encountered in the production of synthetic rubbers applied equally well for these latter.

Isoprene was prepared by Tilden by passing rubber distillation products or turpentine vapours through red-hot tubes. Hoffman [14] hydrogenated *p*-cresol to methyl cyclohexanol, which was then oxidized to methyl adipic acid. This was converted into the diamide and then to the diamine, which was methylated. This diquarternary ammonium base was distilled to yield a pure isoprene. It is interesting to observe that even at this early stage the possibility of obtaining isoprene from petroleum had been studied. Thus Holt [17] obtained isopentenes from

the pentane fractions, converted them into dihalides and then direct to isoprene.

Butadiene was extremely difficult to obtain. An interesting early method was that of Berthelot,[5] who passed a mixture of acetylene and ethylene through heated tubes. Incidentally this work has recently been investigated again by Naragon, Burke and Laukelma,[23] who passed ethylene and acetylene in the presence of steam through a tube at 610° C. obtaining chiefly butadiene. The method developed by Hoffman for isoprene was also used for butadiene except that phenol was the starting material. Matthews and Strange used the butyl alcohol method already described. Harries had a somewhat similar method starting from secondary butyl alcohol. These methods led to the really valuable methods based on alcohol, which will be described in due course. It is quite evident that none of these methods was suitable for the production of the quantities of monomers required for large-scale production of synthetic rubbers.

The Russian chemists, notably Lebedev and Ostromislensky, were making great advances. The former had found that butadiene could be polymerized to give a rubbery material, and he had also observed that substitution in the butadiene molecule had a profound influence on the rate of polymerization. The nature of the rubbery material formed depended on this substitution. Ostromislensky [25] published a book on his researches. He described a number of procedures for the preparation of isoprene by the removal of the elements of hydrogen chloride from the chloroisoamylenes and from 1,3-dichloropentane, but, in so far as the preparation of conjugated dienes is concerned, his attention seems to have been directed chiefly to butadiene. He investigated many cracking processes for the preparation of butadiene and concluded that at a high temperature all open-chain olefines and saturated cyclic hydrocarbons can be cracked to form butadiene and a saturated hydrocarbon. He also prepared butadiene by the catalytic removal of water and an acid from esters of di-glycols, of hydrogen chloride and water from chloroethers, of alcohol and water from acetals, etc. Ostromislensky [27] was the pioneer of a process which was the forerunner of some of the most modern methods. He passed a mixture of alcohol and acetaldehyde over a strongly heated catalyst such as kaolin, condensation and dehydration occurring at the same time, butadiene being formed thereby. He was also carrying out the extensive programme of work on polymerization of vinyl chloride, on which its present ever-growing application is based. In fact with the passing of time, it begins to appear that Ostromislensky is the outstanding figure in synthetic rubber history.

Thus in a patent, Ostromislensky[26] stated that polymerized vinyl chloride or bromide were identical in all properties with the chloride or bromide of butadiene rubber. The action of sunlight caused complete polymerization. The reaction velocity was appreciably accelerated by using ultra-violet light and excluding air. Decomposition was averted by stirring strongly. He found that by heating solutions of vinyl chloride or bromide with zinc dust in the presence of alcohol he obtained the first member of a series homologous with that of natural rubber. Treatment of the polymerized vinyl halides with aromatic amines or caustic potash produced reactions analogous to those produced when butadiene halides were similarly treated.

Synthetic Rubber during the 1914–18 War. The 1918 war provided the first real opportunity of testing the possibilities of synthetic rubber-like materials. All the work was carried out by the Germans under duress. No natural rubber was permitted to enter the country. Faced with an acute shortage of the strategic material, they were forced to inaugurate large-scale production of synthetic material. When this manufacture was actually commenced, it was based oddly enough not on the raw materials which had been so extensively studied in the preceding years in Germany, but upon the much earlier work of

$$\underset{\text{Acetone}}{CH_3—CO—CH_3} \xrightarrow{\text{Magnesium amalgam}} \underset{\text{Pinacone}}{CH_3—\underset{CH_3}{\overset{OH}{C}}—\underset{CH_3}{\overset{OH}{C}}—CH_3}$$

$$\xrightarrow{\text{dehydrate}} \underset{\text{Dimethylbutadiene}}{CH_2{=}\underset{CH_3}{C}—\underset{CH_3}{C}{=}CH_2}$$

FIG. 9.

the Russian, Kondakoff. Their starting material was not isoprene, nor yet butadiene, which had monopolized so much attention, but dimethyl butadiene. Actually this was quite logical, because the latter material could be relatively easily obtained. Its production was based on pinacone which could be obtained from acetone, which in turn was made without great difficulty from calcium carbide. Pinacone was produced by reducing acetone with magnesium amalgam; two molecules of water were then removed by passing pinacone over heated dehydrating agents such as potassium bisulphate or clay.

Two leading types of synthetic rubber were manufactured by the

Bayer Company at Leverkeusen, known as Methyl Rubber H and Methyl Rubber W respectively.

Methyl H was manufactured by placing dimethyl butadiene in metal drums allowing plenty of air space over the liquid. It was maintained at 30° C. for about three months, after which time the liquid raw material had been transformed into a white solid crystalline product which became rubbery when milled. Small quantities of the finished product behaved as a very efficient catalyst for subsequent batches of material. This material yielded reasonably good hard products with good electrical properties. The physical properties were inferior to those of rubber.

The other product, Methyl Rubber W, was produced by heating dimethyl butadiene under pressure at 70° C., for long periods of time—six months or more. In due course the yellow rubbery product which was formed had to be cut out of the containers, a process involving some difficulty. It could be mixed and compounded in the usual manner. It was unsatisfactory as a substitute for rubber. The slow and laborious procedure involved in these forms of production made it fairly evident that there were no great prospects of these materials achieving any profound commercial significance. Another grade of methyl rubber was made at Ludwigshafen by the Badische Anilin und Soda Fabrik by the polymerization of dimethylbutadiene by means of metallic sodium in an atmosphere of carbon dioxide. Although this did not give stronger vulcanized products than Methyl Rubber H, it had an advantage over the latter in being more readily worked on the mill and giving a smooth product which could be extruded more easily.

Both Methyl Rubber H and Methyl Rubber W could be compounded and processed in the usual manner. According to Gottlob,[8] Methyl Rubber H was used for soft rubber goods, for packings, and so on. The working properties of both were not really satisfactory, and the vulcanization products were comparatively feeble compared with natural rubber. According to Gottlob production actually reached the order of 300 tons a month, and in all some 2,350 tons were made and used. Yet it is quite clear that they were quite unsatisfactory, for no sooner was natural rubber available once again than production ceased.

A careful examination of the products of these materials was subsequently carried out by Whitby and Crozier.[42] They concluded that the products were far inferior to those obtained from natural rubber. Methyl Rubber H was found to yield vulcanized products which were only one-third as strong and extensible as compared with rubber products. The Methyl Rubber W, although its extensibility was good, had

only one-tenth of the strength of comparable natural rubber. Both types were very sensitive to temperature changes, were much more loggy and possessed much less nerve than products obtained from raw rubber.

REFERENCES

[1] Bouchardat, *Compte rend.*, 1879, **89**, 1117.
[2] —— *Bull. Soc. Chem.*, 1875, **24**, 108.
[3] Bassett and Williams, *J. Soc. Chem. Ind.*, 1932, **51**, 1215.
[4] Bayer and Co., G.P. 250,690/1909.
[5] Berthelot, *Ann. Chim.*, 1867, **9**, 466.
[6] Carothers, *J. Amer. Chem. Soc.*, 1930, **52**, 5279; 1931, **53**, 4703; 1932, **54**, 1559.
[7] Fernbach, 15,204/1911.
[8] Gottlob, *I.R.J.*, 1919, **58**, 305 *et seq.*
[9] —— *Technology of Rubber*, London, 1927, p. 22.
[10] Harries, *Ann.*, 1911, **383**, 157.
[11] Harries, " Untersuchungen . . .," Berlin, 1919.
[12] Harries and Bayer Company, U.S.P. 1,058,056/19.
[13] Himly, *Ann.*, 1838, **27**, 40.
[14] Hoffman, G.P. 231,806/1909.
[15] Hoffman and Coutelle, G.P. 250,690/1909.
[16] Holt, *Z. Angew. Chem.*, 1914, **27**, 153.
[17] —— U.S.P. 1,189,110/1916.
[18] Kondakoff, *J. prakt. Chem.*, 1900, **62**, 172.
[19] Kyriakides and Earle, *J.A.C.S.*, 1914, **36**, 1004.
[20] Lebedev, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949.
[21] Matthews and Strange, B.P. 24,790/1910.
[22] Memmler, *Chemistry of Rubber*, Reinhold, New York, 1935, p. 242.
[23] Naragon, Burke and Laukelma, *Ind. Chem. Eng.*, 1942, **34**, 355.
[24] Oenslager and Marks, *Ind. Eng. Chem.*, 1925, **17**, 393.
[25] Ostromislensky, *Caoutchouc and Its Analogues*, Moscow, 1913.
[26] —— G.P. 264,123/1912.
[27] —— *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1472, 1911, 1960.
[28] Perkin, *J. Soc. Chem. Ind.*, 1912, **31**, 662.
[29] Perkin, Weizmann, Matthews and Strange, B.P. 5932/1910; 13,051/1912
[30] Pickles, *J. Chem. Soc.*, 1910, **95**, 1086.
[31] Schotz, *Synthetic Rubber*, Benn, London, 1926.
[32] Staudinger, *Ann.*, 1926, **445**, 97.
[33] —— *Kautschuk*, 1927, **3**, 63.
[34] Thiele, *Ann.*, 1889, **308**, 337.
[35] —— *Ann.*, 1901, **319**, 226.
[36] Tilden, *Chem. News*, 1882, **46**, 120.
[37] —— *Chem. News*, 1892, **65**, 265.
[38] —— *J. Chem. Soc.*, 1884, **47**, 411.
[39] Wallach, *Ann.*, 1887, **239**, 48.
[40] Weizmann, B.P. 4845/1915.
[41] Whitby, *Trans. I.R.I.*, 1929, **5**, 184.
[42] Whitby and Crozier, *Can. J. Research*, 1932, **6**, 203.
[43] Whitby and Katz, *J. Amer. Chem. Soc.*, 1928, **50**, 1160.
[44] Williams, *Proc. Royal Soc.*, 1860, **10**, 516.

CHAPTER 5

CHEMICAL BEHAVIOUR AND STRUCTURE OF NATURAL RUBBER

In so far as it has had a very profound effect on the problem of making synthetic materials, the structure of rubber is of considerable importance. Much of the evidence regarding this has been derived from its chemical behaviour. The following account gives a brief résumé of the present position.[1, 2]

Owing to its unsaturation, rubber is a very reactive material. This is responsible for many of its disadvantages. In this respect many synthetic elastic materials are of value precisely because they do not undergo these chemical changes. This chemical reactivity has also enabled a considerable amount of work to be carried on towards elucidating its structure.

While much of the work has been directed towards elucidating the structure of rubber, many new materials have thus been obtained. Some have become important materials of commerce. The abundant supply of rubber since 1930 and the low price made it attractive as a raw material and resulted in the commercial development of some of these derivatives.

By processes of cyclization, chlorination, and hydrochlorination, natural rubber was converted into products with great hardness and rigidity, and increased resistance to moisture and corrosive influences. These products have found many uses in protective coatings of the paint and lacquer type, in wire-insulation compositions, as films for packaging foods and other products, as paper coatings to reduce moisture penetration, as adhesives, and in a number of other applications.

The singular feature about all the many interesting products is that as the degree of unsaturation is reduced, the elastic properties tend to disappear, so that in many cases these are completely absent, the product being invariably thermoplastic. Many of these synthetic thermoplastic materials have already found wide commercial application. They illustrate the other side of the picture, the approach of rubber to plastics. Already similar derivatives are being produced from butadiene elastomers, from polyisobutylene, etc.

Rubber and the Halogens. Rubber hydrocarbon is unsaturated and behaves like a typical olefine. Thus it reacts very readily with halogens and halogen acids ; for example, it readily takes up chlorine,

as was first shown in 1859 by Englehard and Day.[15] Not much interest was taken in this material until 1915, when Peachey [34] was able to obtain a product containing 65 per cent. of chlorine. Theoretically, rubber should only yield a product of 51 per cent. of chlorine by addition, so that considerable substitution takes place as well.

In recent years there has been a great deal of activity with chlorinated rubber, which is of great commercial value owing to its ability to dissolve in many solvents from which films may be obtained having great resistance to corrosion. It withstands both acids and alkalies. Films from it are unaffected by water, steam, sunlight, oxygen, etc.

One of the main trends has been to depolymerize the rubber prior to chlorination, making use of every method for degrading it.[7, 11, 12, 13, 24] This has been effected either by excessive milling causing mechanical breakdown, or by the use of ultra-violet light or sunlight, or by the addition of oxidizing agents, or by the use of small quantities of the deleterious metals—copper, manganese, cobalt, etc. The material is available in several forms, giving solutions of different viscosity.

Films of chlorinated rubber are quite brittle and show no elasticity whatever. They have to be plasticized with materials such as chlorinated diphenyls, coumarone resins, dibutyl phthalate, tricresyl phosphate, etc. There is considerable literature on the subject both technical and commercial. Chlorinated rubber structurally is of considerable interest in relation to other chlorinated elastic materials such as chloroprene and polyvinyl chloride.

In connection with synthetic elastic materials it is of great interest, as wherever bonding to metal is required, that a solution of chlorinated rubber is frequently employed with great success, e.g. for Buna S, Perbunan, neoprene, Hycar, etc. It is also miscible with polyvinyl resins and polyacrylic esters.

Gladstone and Hibbert,[20] in addition to their work with chlorinated rubber, examined the behaviour of rubber with bromine, and obtained a fully saturated compound, $C_{10}H_{16}Br_4$, which corresponded with the addition of bromine at the double bond.

The behaviour of rubber with halogen acids corresponds closely to its behaviour with the halogens themselves. Weber [47] obtained white products approximating to a composition of C_5H_8HCl. Harries [22] prepared the corresponding hydrogen bromide derivative and obtained a material whose formula corresponded to $(C_5H_8.HBr)_x$.

In recent years, as the result of work carried out by Bradley [3] and McGavack, commercial derivatives of some potential importance have been obtained from rubber hydrochloride.

If hydrogen chloride is passed into a solution of rubber at ordinary

temperatures, a white solid product is obtained which can be easily separated. This is rubber hydrochloride. Calvert[9] showed how, when suitably stabilized, it can be converted into films and sheets having wide commercial application.

This has been marketed by the Goodyear Company as *Pliofilm*. It is transparent, tasteless, and odourless. It is strong, can be stretched, is resistant to tear, is moisture proof, and resistant to oils and greases. Its thermoplastic character is illustrated by the fact that it can be heat sealed at 105° C., a fact of some importance for many applications.

Influence of Oxygen. Oxygen plays a dominating part in the behaviour of rubber. Many of the disadvantages of rubber are attributed to its vulnerability towards oxygen. Raw rubber tends to take up oxygen; it sometimes oxidizes during storage, becomes very tacky, and can change to an almost unrecognizable inelastic resinous mass. This is due to the presence of oxygen which promotes changes in its structure. The effect is assisted by the presence of substances which catalyse the oxidation process. It is also aided by increase in temperature and by exposure to ultra-violet light. Oxygen makes vulcanized rubber perish and lose its valuable mechanical properties.

In recent years it has been conclusively established that oxygen plays a vital rôle in rubber behaviour. It is thought to have a profound influence on such phenomena as tackiness,[8] mastication behaviour,[10] structural changes, etc. Many investigations have shown that rubber takes up oxygen during oxidation although the quantity is very small. It has always been a mystery why such small quantities of oxygen should be able to exert such a profound effect on solution properties and mechanical properties. The explanation put forward by Staudinger and Leopold[41] is the most plausible so far, based on the macromolecular theory. Assuming a rubber molecule to be very long, made up of, say, 1,000 isoprene units as a polymerization chain, then oxygen may affect it in this way—

$$(C_5H_8)_{1,000} + O_2 \rightarrow 2(C_5H_8)_{500}O$$

The molecules formed will be considerably shorter, and will thus tend to give lower viscosity and modified physical properties. Evidently, viewed in this manner, very minute amounts of oxygen will profoundly alter the rubber. This appears also to be the case with some synthetic products, notably Buna S.

The outstanding feature about other oxidizing agents in relation to rubber is the use of benzoyl peroxide. Ostromislensky[32] in 1915 found that this produced a vulcanizing or setting action on rubber without involving the customary use of sulphur. This work led up to the

extended successful use of benzoyl peroxide and similar materials as polymerization agent for many synthetic elastics and ethenoid resins notably by Klatte and Rollett.[27] In contrast to this it has recently been found that small amounts of benzoyl peroxide have a profound depolymerizing action in masticating rubber; this seems to be a function of temperature.

Harries [23] found that oxidizing agents such as alcoholic potassium permanganate solution converted rubber into a thick syrup, which was still $(C_5H_8)_x$. His inference was that the rubber had depolymerized.

The deliberate resinification of rubber by oxygen has resulted in the formation of interesting commercial materials known as *Rubbone*. Stevens [43] treated well-masticated rubber in solution in white spirit, with small amounts of cobalt linoleate. When air was passed through this for eight hours at 80° C. a resin was obtained which has found application for paints and lacquers. As described by Stevens and Stevens,[44] it is a pure thermo-setting resin having the composition $(C_5H_8)_2O$. It has no elastic properties but is very resistant to corrosion.

Cyclo-Rubbers. The work so far described has been largely concerned to establish that rubber is an open-chain material. In recent years a great deal of work has been carried out to convert rubber into isomeric compounds. These, while still having the same empirical formula as rubber, nevertheless are much less unsaturated and differ considerably in properties. The lower unsaturation is attributed to cyclization within the molecule. For this reason they are often referred to as cyclo-rubbers. The behaviour described has a considerable bearing on the polymerization of butadiene and its derivatives, particularly in relation to the processing properties.

The iso-rubbers made by Harries have already been mentioned. Staudinger [39] has produced numerous cyclo-rubbers by reducing rubber or rubber hydrochloride in toluene with zinc dust. Staudinger and Geiger [42] heated rubber above 250° C., so that cracking was avoided. They found that the degree of unsaturation decreased. They considered that a cyclo-rubber had been formed. The cyclic product contained only one double bond for every five isoprene units, four of which had combined to form a ring. Its appearance had changed, for it was a light yellow powder without rubbery properties. Its density was greater. Staudinger's macromolecule or long-chain theory of the structure of rubber was largely based on this work. He thought rubber was made up of enormously long open chains of isoprene units. The tendency for cyclization among the repeating groups at different positions accounted for his different cyclo-rubbers.

Fisher[18] in 1927 showed that rubber behaves in a remarkable manner when treated with concentrated sulphuric acid. He was able to obtain a number of thermoplastic materials merely by milling rubber with sulphuric acid. Tough materials which could be rendered plastic with heat could be obtained when rubber was milled with 5 per cent. of concentrated sulphuric acid, and thereafter heated at 130° C., for about fifteen hours. Kirchhof[26] independently arrived at the same conclusions working on rubber solutions. When the method was developed by replacing sulphuric acid with sulphonic acids, a number of most useful materials became available. Fisher milled rubber together with organic sulphonic or chloro-sulphonic acid or sulphonyl chloride. The materials when subsequently heated were tough and thermoplastic, in some instances resembling shellac, and others resembling balata or gutta-percha. These are the commercial *thermoprenes*, which are very extensively used as adhesives.

According to Fisher[19] the nature of the products varied with the temperature and the time of reaction. The products have characteristics which enable them to be grouped as—

(*a*) Somewhat resilient materials which resembled vulcanized rubber.

(*b*) Hard tough thermoplastics resembling balata and gutta-percha.

(*c*) Hard brittle materials resembling shellac.

The various products were all much less unsaturated than rubber, the value decreasing as low as one-third of the unsaturation of rubber. They could be vulcanized to give products somewhat similar to those obtained from raw rubber.

It is interesting to observe that these synthetic isomers of rubber in many respects resemble the natural isomers, balata and gutta-percha.

Rubber and Metal Halides. The behaviour of rubber towards reactive metal halides is very interesting. By treating anhydrous rubber solutions with materials such as stannic chloride, ferric chloride, antimony chloride, etc., Bruson, Sebrell and Calvert[4] obtained coloured products which broke up in alcoholic acetone to yield hydrocarbons in many respects similar to thermoprenes. The stannic chloride addition product had the composition $(C_5H_8)_{10}\ SnCl_4$. When decomposed, this gave a white powder which was $(C_5H_8)_x$.

Bruson[5] was able to obtain interesting commercial materials by adding about 10 per cent. of chloro-stannic acid, either direct to rubber on a mill or to a benzene solution of rubber. The products contain a certain amount of bound chlorine. These are the basis of the *Plioform* resins which have come into industrial use.

The members of this group are all thermoplastic. They are resistant

to most acids, alkalies, and many solvents. They withstand water, and have excellent electrical properties.

According to Winkelman and Jones,[48] amphoteric metal halides seem particularly effective in producing thermoplastic materials from rubber. Thus 10 parts of ferric chloride milled into 100 parts of rubber and heated at 100° C. for fifteen hours gave a hard brittle thermoplastic material.

All these products are cyclo-rubbers. In the main they tend to be more plastic than elastic, and in this respect tend to resemble the ethenoid type of elastic materials.

It has also been found that the halogen compounds of non-metals have a profound cyclizing effect on rubber. Boron and phosphorous compounds are outstanding in this respect. This is particularly interesting in view of the influence of these materials on the polymerization of isobutylene for example. Bruson [6] found that boron trichloride converted rubber in benzene into a white powder. He also showed that boron fluoride and fluoboric acid reacted with rubber on the mill to give thermoplastic cyclo-rubber. Stevens found that 2 to 3 per cent. boron trifluoride or 8 per cent. fluoboric acid on the rubber gave hard flexible materials which were partly cyclized rubbers and could be vulcanized. Farmer, Rowe and Stevens [16] obtained various cyclo-rubbers by the use of fluorine compounds of boron and phosphorous. Reaney [36] prepared cyclo-rubbers by milling phosphorous pentachloride into rubber which contained aluminium sulphate; the mass was then heated at 160° C. for some hours.

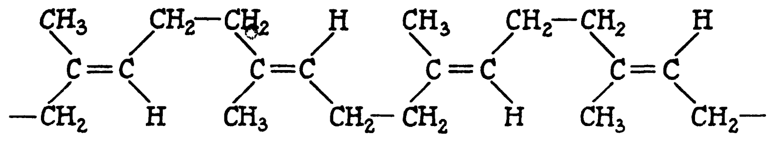
It is interesting to note that sulphur chloride has a profound effect on rubber, being the basis of the cold cure, or low-temperature vulcanization of rubber. This was discovered by Alexander Parkes [33] in 1846. The action is extremely rapid, but whereas other cyclizing agents give thermoplastic materials, sulphur chloride yields elastic products; so that sulphur chloride certainly only results on partial cyclization.

In passing it is interesting to observe that those concerns who have led in the production of cyclo-rubbers are also prominently concerned with the production of synthetic elastics.

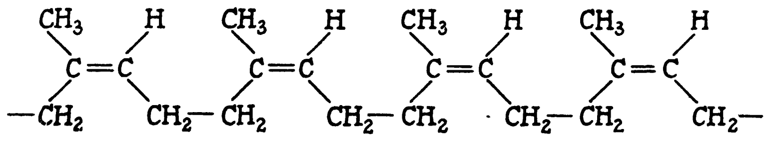
Chemical Derivatives of Synthetic Isoprene Rubbers. A process for cyclizing synthetic polyisoprene in the same way as a natural rubber was developed to give a product which, for many applications, is equivalent to cyclized natural rubber. American products of this type include Plolite S1 and Plolite S2. These are made by the action of chlorostannic acid on polyisoprene. GR-S does not react under the same conditions. A process for chlorinating synthetic polyisoprene was developed which gives a product similar to chlorinated natural

rubber with respect to chlorine content, viscosity, thermal stability, solubility and general utility in protective coatings and rubber-to-metal adhesives. GR-S cannot be satisfactorily chlorinated under the same conditions.[14] Synthetic polyisoprene readily adds hydrogen chloride in a manner similar to natural rubber, whereas GR-S is practically unaffected. The product, however, does not have the excellent film-forming properties of Pliofilm. The striking similarity in chemical behaviour of synthetic polyisoprene and natural rubber is attributed to the common chemical structure. The relative chemical inertness of GR-S is attributed to lack of a methyl group attached to double bond.

Structure of Rubber. So far as the chemical structure of rubber is concerned, current opinion favours Staudinger's theory of macro-



Gutta-percha 'cis' form



Rubber 'trans' form

FIG. 10.

molecules or giant molecules. This has been supported by X-ray examination of rubber. Katz [25] showed that stretched rubber has an orderly structure. Thus he obtained a diagram from stretched rubber but not from rubber in the unstretched state. Meyer and Mark [29] by X-ray measurement found that the results corresponded with an isoprene unit as being the chief constituent of the main valency chain.

It is singular that gutta-percha, which is a natural isomeric form of rubber, shows many chemical reactions similar to rubber, but lacks elasticity. Staudinger [38] has suggested that the difference may be due to a different space arrangement of the molecule, rubber being the *trans* form, and gutta-percha being the *cis* form. It is interesting to note, according to Ferri,[17] that gutta-percha, when heated with cyclizing agents, give the same products as are obtained from rubber.

Molecular Weight of Rubber. The molecular weight of rubber has so far not been conclusively determined. It would be extremely valuable information, for it would determine the length of the molecule, and would then explain much of its behaviour.

In his work on rubber ozonides, Harries found that the freezing-point depression in benzene solution corresponded to a formula $C_{25}H_{40}$. Pummerer [35] estimated the molecular weight of rubber to range between 1,400 and 2,000 on the basis of the lowering of the freezing-point in camphor. In this case the rubber molecule would contain from 15 to 30 isoprene units. Staudinger [40] found that hydrogenated rubbers had molecular weights from 3,000 to 5,000. This suggested that rubber would be much higher, as it would inevitably break up during hydrogenation. He estimated the length of the rubber macromolecule at 8,100 Ångstrom units. On the basis of osmotic pressure measurements of rubber in benzene, Meyer and Mark [30] considered the molecular weight to be as high as 250,000. Schade [37] has summarized the position by the comment that calculations indicate that from 200 to 4,400 C_5H_8 units for the rubber molecule according to the treatment to which it has been submitted.

Elastic Properties. So far as the structure of rubber in relation to its elastic properties are concerned, there has been the greatest confusion.

Treloar [46] has summarized admirably the prevailing current ideas regarding the structure of rubber. Rubber-like elasticity is definitely associated with materials having very long chains of atoms.. The dynamic interpretation of elasticity in rubber is widely accepted. The idea was introduced by Meyer, von Susich and Valko,[31] and developed by Guth and Mark,[21] and Kuhn.[28]

Rubber is accepted to consist of long-chain molecules. It is assumed that the carbon atoms in this chain are in a state of continuous thermal vibration. Each C—C bond may be regarded as rotating freely about the preceding bond as axis. As a result the chain will not be uniform zig-zag in one phase, but will be kinked at random in three dimensions. The distance between the ends of the chain will tend to be less than in the regular zig-zag. The probable end-to-end length can be calculated by statistical methods. It is found to be proportional to the square root of the number of links in the chain, or to the molecular weight.

If the randomly kinked molecule is forcibly stretched and then released, the active thermal motion will tend to restore it to a length approximating to the probable statistical length. In other words, it shows elastic behaviour.

To confer elasticity on bulk material Treloar states three requirements:

(*a*) The presence of long-chain molecules with freely-rotating links.

(*b*) Weak secondary forces around these molecules, i.e. one molecule will not unduly influence the adjoining ones.

(*c*) A few points of cross linking, resulting in a loose three-dimensional network.

Treloar gives the following explanation of the necessity for cross-linking.

For the rubber to be able to maintain any sort of permanent shape the molecules must be fixed in their *average relative* positions. It is necessary to regard the individual molecules as being joined together by a small number of unbreakable bonds. These should be enough to make a three-dimensional network. But the individual molecule chain is so long that these few links will not impede the free movement of the parts of the molecule chain between the links.

In practice, rubber-like properties appear only within a certain range of temperature. At low temperatures rubbers are transformed to a glass-hard condition. Below the transition temperature the molecular chains become immobile, the thermal energy no longer being sufficient to overcome the secondary forces between the molecules. For a material like natural rubber these secondary forces are relatively weak, and the transition temperature is very low (– 70° C.). If the intermolecular forces are comparatively strong, the transition temperature is very much higher. This is exemplified by polymethacrylate, which is a glass at normal temperatures, but becomes highly elastic above about 70° C.

Rubber-like properties may disappear at high temperatures, where, in the case of polymers which are not cross-linked, the molecules become sufficiently mobile to slide bodily past one another, the rubber thus becoming a viscous liquid. The longer the molecules, the higher the temperature at which this effect becomes noticeable. Such plastic flow occurs in raw rubber in which there are no true cross-links between molecules, but only what may be called entanglement-cohesions, i.e. complex mechanical entanglements held together with varying degrees of permanency by the secondary forces.

The rubber-like state is thus limited at low temperatures by the magnitude of the secondary forces tending to produce complete rigidity, and at high temperatures by the strength of the intermolecular cross-links, responsible for the maintenance of the structure.

It is now widely accepted that rubber may contain a crystalline phase. The chief evidence for this is in the X-ray patterns which are

formed. It is not possible to identify the usual precise geometrical forms of crystal in rubber. From the angle of synthetic rubbers it is important that neoprene and butyl rubber also show evidence of a crystalline phase. The others do not and many differences of behaviour may be explained by this.

Treloar has pointed out that the essential attribute of a crystal is the internal regularity of the spacing of its constituent atoms. Any external geometrical regularity is dependent on this fundamental internal regular structural. However, internal regularity is not always accompanied by external regularity. Thus metals are invariably crystalline. The absence of external regularity is due only to the small size of the individual crystallites. The same considerations apply to rubbers.

Highly-stretched crystalline rubber possesses many of the characteristics of fibrous materials. It may readily be torn along the direction of the extension, but is extremely tough in directions at right angles. Hock showed that if frozen in liquid air and hammered, it splits up into fibres.

Raw rubber may be crystallized either by *freezing or by stretching.* Whereas liquids generally crystallize almost instantaneously, rubber crystallizes very slowly. According to Treloar, crystallization in the unstretched state takes about 10 days at 0° C., but is more rapid at lower temperatures, taking only a few hours at 20° C. At still lower temperatures the rate of crystallization is again reduced, and at temperatures below 40° C. there is no crystallization at all.

There are other important differences between the crystallization of rubber and of low-molecular liquids. Crystalline rubber does not "melt" at a sharply defined temperature, but over a range of about 10° C. The melting temperature depends entirely on the temperature at which crystallization is effected, being lower the lower the temperature of crystallization. Crystallization in rubber is never complete, and the percentage of crystalline material increases slowly over a period of years. According to Treloar, there is a corresponding increase both in the value and in the definiteness of the melting temperature, pointing to an increasing stability of the crystalline state with the lapse of time.

These effects, and the dependence of the melting temperature on the conditions under which crystallization occurs, point to the absence of a true equilibrium between the crystalline and amorphous components in the rubber.

There are some similarities between the crystallization process in rubber and in low-molecular liquids.

Treloar has shown that crystallization is accompanied by the

evolution of heat (latent heat) and by a change (usually an increase) in density. Again, just as many crystals are doubly refractive (or bi-refringent), so are the crystals in rubber. He has employed both the change in density and the bi-refringence to obtain a quantitative measure of the amount of crystalline material present in a given piece of rubber.

X-ray Evidence. The most definite evidence on the existence of crystals in rubbers comes from the observation of the diffraction pattern produced by X-rays. There are four distinct types of pattern, associated with specific types of structure. These are :

(1) *Single Crystal.* A single crystal, representing the highest state of ordered arrangement, gives a pattern of sharp spots, arranged in a geometrical order. From the analysis of the positions and intensities of the spots, the relative positions of the atoms in the structural "lattice" of the crystal can generally be calculated.

(2) *Powder (or Polycrystalline Solid).* The powder, or polycrystalline solid, having crystal directions arranged at random, gives rise to a characteristic pattern of sharply defined circles. With very small sizes of crystallite the rings become diffused until ultimately it approaches (3).

(3) *Liquid (or Glass).* A liquid or glass is characterized by a more or less random arrangement of atoms. The only difference (structurally) between these two states is that in a glass the positions of the atoms are fixed, whilst in a liquid they are continually fluctuating. The X-ray diffraction pattern consists only of one or more broad haloes. These arise from the fact that although the structure is random, there is nevertheless a tendency for certain interatomic distances to occur more frequently than others.

(4) *Fibres.* Natural and artificial fibres (wool, silk, nylon, etc.) give a pattern in which the number of spots is generally not so great as in (1), and the spots are arranged in a characteristic manner. There is also usually a diffuse background like that in (3). This type is due to the presence of crystallites all oriented more or less along the fibre axis ; together with a component of non-crystalline "amorphous" molecules. The analysis of the crystal structure is considerably more difficult than is the case with (1).

X-ray examination of rubber shows :

(*a*) Ordinary unstretched raw or vulcanized rubber gives the liquid pattern (3). Rubber cooled rapidly to below $-70°$ C. and brought to the brittle or glassy state gives an identical pattern.

(*b*) Crystalline unstretched rubber gives a pattern of rings like (2) above. This is accompanied by a background of the type

(3), showing the existence of a polycrystalline phase, together with an amorphous component.

(*c*) Stretched rubber gives the fibre pattern (4). Field suggested that in the most highly stretched rubber the proportion of the crystalline phase is about 80 per cent.

Molecular Structure of Crystalline Rubber. It is possible to estimate the size of the crystallites in crystalline rubber from the size of the spots in the X-ray fibre pattern. According to Treloar, they are found to have a length of about 600 Ångstrom units (6×10^{6} cm.). The average length of a molecule in raw rubber being 20,000 Å (0·0002 cm.), it follows that the average molecule must pass alternately through several crystallites. The structure of crystalline rubber must therefore be something like a number of separate crystallites tied together by lengths of molecules which cannot be fitted into a neighbouring lattice, and which provide the amorphous component whose presence is also revealed by the X-ray photographs.

Stretching forces the molecules into a state of alignment in which less rearrangement is required for crystallization. The two phenomena, crystallization by freezing and crystallization by extension, are not two distinct processes, but a single process occurring under different physical conditions, between which a continuous gradation may be observed.

At sufficiently low temperatures the molecular mobility may be reduced to such an extent that crystallization does not occur in any reasonable time. That is why rubber cannot be crystallized at temperatures below $-40°$ C.

The introduction of permanent cross-links between the molecules, as in vulcanization, reduces their mobility and thus slows down the rate of crystallization. It also reduces or eliminates plastic flow.

Mechanical Effects of Crystallization. Since a number of molecules become locally associated in the crystallite, crystallization effects a kind of cross-linking between molecules, akin to vulcanization. The effect is strikingly exhibited in raw rubber, in which the rate of plastic deformation at first rises with increasing extension, then begins to fall again as the extension is further increased. Treloar concluded that mechanical entanglements, which are responsible for the maintenance of the network structure of raw rubber, become of less importance at high extensions, their function being taken over by the more effective binding of the molecules in the crystal lattices. The same effect is undoubtedly responsible for the very high tensile strength of vulcanized rubber. GR-S, which, like all copolymers of irregular molecular structure, cannot crystallize, has a very much lower tensile strength.

Raw GR-S, when stretched, yields continuously right up to the breaking-point.

A complete new orientation of ideas has come about in connection with the work on synthetic rubber. The clearest and most cogent exposition of the position has been made by Thomas, Lightbown, Sparks, Frölich and Murphree [45] as follows:

The tradition that rubber properties were related to high unsaturation persisted and has led to numerous theories of elastic behaviour based on geometric structures resulting from unsaturated linkages. Whitby and Staudinger questioned the importance of unsaturation in determining rubber-like behaviour but encountered some difficulty in finding adequate support for this view, owing to the poor elastic properties of the practical examples available to them. Our studies on polymers of the simple mono-olefines, which have been in progress for the past ten years, have led to some interesting conclusions in regard to this point. It was shown that high-molecular-weight linear polymers derived from simple olefines, such as the butylenes, possess a majority of the properties characteristic of rubber. Only the susceptibility to chemical action can definitely be attributed to the unsaturation of the natural rubber molecule. Physical properties which appear not to be intrinsically dependent upon the carbon-double bond-carbon configuration are: tensile strength, elasticity, rebound, elastic memory, X-ray structure, mechanical orientation, electrical properties, and fractional solubility. It was, however, conclusively demonstrated that the saturated polymers are not capable of vulcanization in conventional manner.

From these and other studies it is concluded that the chemical unsaturation, which is so important from the standpoint of permitting vulcanization to take place, is also the greatest weakness of the natural rubber molecule. The reason for this is that in the case of soft goods, which represent by far the major outlet for rubber, only a fraction of the available double bonds is utilized in the vulcanization with sulphur. The low but definite consumption of unsaturation during vulcanization of rubber was first pointed out in 1912 by Spence and Scott. Their conclusions were further confirmed by Boggs and Blake and by Brown and Hauser. The latter showed that there is evidence of overcuring after as little as 2 to 3 per cent. of the unsaturation has been used up. The large residual unsaturation is responsible for the pronounced chemical reactivity of soft rubber goods. It is this unsaturated character which makes natural rubber so susceptible to oxidation with consequent deterioration on ageing and disintegration when subjected to the action of ozone. It is also responsible for its lack of resistance to such chemical agents as strong mineral acids, and also to its lack of heat stability under oxidizing conditions.

As a result of this analysis, they have been able to develop new synthetic elastics—butyl rubbers—from which many of the undesirable properties of natural rubber are absent.

REFERENCES

[1] BARRON, *British Plastics*, 1938, **10**, 377 *et seq.*
[2] —— *British Plastics*, 1938, **10**, 420, 520.
[3] BRADLEY and MCGAVACK, U.S.P. 1,519,569/1924.
[4] BRUSON, SEBRELL and CALVERT, *Ind. Eng. Chem.*, 1927, **19**, 1033.
[5] BRUSON U.S.P. 1,797,188/1930.
[6] —— U.S.P. 1,846,247/1932.
[7] Buckau, A. G., B.P. 416,252/1934.
[8] BUSSE, *Ind. Eng. Chem.*, 1932, **24**, 140.
[9] CALVERT, Can.P., 340,261/1934.
[10] COTTON, *Trans. I.R.I*, 1931, **6**, 487.
[11] DOD, B.P. 470,286/1936.
[12] DYKE-TEAGUE, U.S.P. 1,826,275/1931.
[13] —— B.P. 305,986/1929.
[14] ENDRES, *Rubber Chem. Tech.*, 1944, **17**, 403.
[15] ENGLEHARD and DAY, B.P. 2734/1859.
[16] FARMER, ROWE and STEVENS, B.P. 467,531/1937.
[17] FERRI, *Chim. Helv. Acta.*, 1938, **20**, 149.
[18] FISHER, *Ind. Eng. Chem.*, 1927, **19**, 1325.
[19] —— U.S.P. 1,642,018/1927.
[20] GLADSTONE and HIBBERT, *J. Chem. Soc.*, 1888, **53**, 682.
[21] GUTH and MARK, *Monatsh.*, 1934, **65**, 92.
[22] HARRIES, *Ber.*, 1904, **87**, 2708.
[23] —— *Untersuchungen* . . ., Leipzig, 1919, p. 99.
[24] I.G., B.P. 390,097/1932.
[25] KATZ, *Chem. Ztg.*, 1925, **49**, 353.
[26] KIRCHHOF, *Kautschuk*, 1926, **2**, 1.
[27] KLATTE and ROLLETT, U.S.P. 1,241,738/1917.
[28] KUHN, *Koll. Z.*, 1936, **76**, 258.
[29] MEYER and MARK, *Ber.*, 1928, **61**, 1939.
[30] —— *Ber.*, 1931, **64**, 1913.
[31] MEYER, VON SUSICH and VALKO, *Koll. Z.*, 1932, **59**, 208.
[32] OSTROMISLENSKY, *J. Phys. Chem. Soc. Russ.*, 1915, **47**, 1892.
[33] PARKES, B.P. 11,147/1846.
[34] PEACHEY, B.P. 1894/1915.
[35] PUMMÉRER, *Zeit. für angew. Chem.*, 1934, **67**, 304.
[36] REANEY, B.P. 459,435/1936.
[37] SCHADE, *R.A.* (N.Y.), 1941, **48**, 387.
[38] STAUDINGER, *Helv. Chim. Acta.*, 1926, **9**, 549.
[39] —— *Berichte*, 1928, **61**, 2575.
[40] —— *Die hochmolekularen organischen Verbindungen*, 1930, p. 380.
[41] STAUDINGER and LEOPOLD, *Trans. I.R.I*, 1934, **10**, 276.
[42] STAUDINGER and GEIGER, *Helv. Chim. Acta.*, 1927, **10**, 530.
[43] STEVENS, B.P. 417,912/1933.
[44] STEVENS and STEVENS, *Trans. I.R.I.*, 1935, **11**, 182.
[45] THOMAS, LIGHTBOWN, SPARKS, FRÖLICH and MURPHREE, *Ind. Eng. Chem.*, 1940, **32**, 1283.
[46] TRELOAR, *I.R.J.*, 1945, **111**, 1320.
[47] WEBER, *I.R.J.*, 1903, **25**, 639.
[48] WINKELMAN and JONES, U.S.P. 1,751,817/1930.

CHAPTER 6

RAW MATERIALS: ALCOHOL AND ACETYLENE

Raw Materials. Many years ago the idea of using isoprene as the fundamental raw material was discarded owing to the apparently insuperable difficulties of obtaining it. Nor has any polymer been obtained from it with physical properties close to those of natural rubber. For years the quest for synthetic rubber hinged on discovering a cheap source of isoprene. Tapping pine trees for turpentine offered no advantage over tapping rubber trees for latex. Nearly all work has been founded on butadiene. It would be foolhardy to assume that this is conclusive. It is not. For isoprene is being made from turpentine on a very large scale by the Hercules Powder Co.[19] It is also being made by the Standard Oil Company from butyl alcohol in large quantities. The amounts involved are larger than the butyl rubber programme requires. Synthetic isoprene rubbers are being made. There is a growing interest in polyisoprene, in copolymers with styrene, and of copolymers with both butadiene and styrene. Fryling [17] has described the recent developments with isoprene rubbers and copolymers.

Quantitative Aspect of Making Butadiene. It is instructive to examine the present requirements for butadiene.

The largest amount of GR-S to be produced involved 688,500 tons of butadiene per year. Figures do not usually mean much unless translated into something that permits a relative comparison. On a volume basis these 688,500 tons of butadiene become 263,300,000 gallons. It is more than twice the amount of ethyl alcohol produced yearly in the United States in normal times. It is more than ten times the toluene output for the year 1939.

Until a very few years ago this chemical, which suddenly has assumed such importance as an essential raw material in the synthetic-rubber programme, was still in the class of laboratory curiosities. The oil industry had long been familiar with butadiene as a constituent of cracked petroleum fractions. In petrol production it was an undesirable constituent. Butadiene and other conjugated diolefines were carefully removed to prevent gum formation in the petrol. There had been so little incentive to work out processes for the recovery of this petroleum butadiene that an American chemist who in the late thirties needed an ounce of reasonably pure material could not find a domestic

supply but had to go out in the laboratory and make it himself by whatever method he could select from the technical literature. Only a few American research organizations interested in synthetic rubber had much first-hand information on its physical and chemical properties. If one turned to the literature, such data as could be found were apt to be contradictory and misleading.

The great problem in the production of butadiene has been to obtain at low cost a molecule of some sort having four carbon atoms in a row. That is why the earlier efforts were based on materials such as butyl alcohol and isobutyl alcohol. For these alcohols, and indeed alcohols in general, can be easily and smoothly dehydrated to yield the respective olefines—butylene and isobutylene in the above cases. Simplifying this, it seems that the key material is actually ethylene.

As Dunstan [11] has put it, ethylene, propylene, butylenes and amylenes " are the authentic chemical bricks of our new synthetic chemistry—the chemistry of rubber, of plastics, and of polymers of various degrees of complexity . . . such chemical bricks are of outstanding importance and value ".

Processes for Manufacturing Butadiene. According to Frölich and Morrell,[16] the most important processes for making butadiene fall into three general classes:

(1) Reactions dependent upon building up the butadiene structure from materials containing only two carbon atoms in the molecule. This class includes synthesis based on the utilization of ethyl alcohol, acetylene, and possibly to some extent ethylene.

(2) Reactions based on the conversion of suitable C_4 compounds into the diolefine structure. Processes of this type are the dehydration of butylene glycols and the removal of hydrogen from C_4 hydrocarbons either by direct dehydrogenation by means of a catalyst, or by chlorination followed by dehydrochlorination.

(3) Reactions involving decomposition of molecules containing more than four carbon atoms, in which class falls the thermal cracking of higher boiling petroleum fractions. This process is inherently one of breaking down longer chain or ring structures under conditions favouring the formation of the conjugated double-bond system.

As already suggested, butyl alcohol was the chief starting-point used by the English workers on synthetic rubber.[36] It was obtained by the Fernbach [15] fermentation process. This fermentation of starches by means of enzymes was developed further by Weizmann,[42] who was a member of the research team led by W. H. Perkin, junior, and which included Matthews and Strange.

Thus secondary butyl alcohol, which is obtainable in fairly large

quantities, can be converted into butadiene without untoward difficulty. It is dehydrated by passing over a catalyst—phosphoric acid—at 450° C., to yield an olefine—butylene. This may be easily brominated. If followed by removing two molecules of hydrogen bromide, the resulting product is butadiene.

$$\underset{\text{Sec. Butyl Alcohol}}{CH_3.CH(OH).CH_2.CH_3} \xrightarrow{\text{dehydrate}} \underset{\text{Butylene}}{CH_3.CH \quad CH.CH_3} + H_2O$$

$$\xrightarrow{\text{bromine}} CH_3.CHBr.CHBr.CH_3$$

$$\xrightarrow{\text{remove 2HBr}} \underset{\text{Butadiene}}{CH_2 \quad CH—CH - CH_2}$$

FIG. 11. Butadiene from Secondary Butyl Alcohol.

The Use of Ethyl Alcohol. Ethyl alcohol has been one of the chief raw materials utilized for the production of butadiene. It has been the basis of many synthetic processes. In view of the importance of alcohol to other chemical industries and the plastic industry, it is worth while closely considering this angle. This use of alcohol to make butadiene had encountered great competition from cheaper raw materials. Alcohol from grain was at one time one of the main planks in the current synthetic rubber production. World food shortages accompanied by correspondingly high prices for cereals of every description have made these sources of alcohol prohibitive. Nevertheless, the time may come when different circumstances will prevail.

For many years alcohol derived from potatoes was the chief starting material used in the U.S.S.R. Since production of synthetic rubber has there been carried out on a large scale, no doubts can be entertained as to its practicability. Its use for making synthetic rubber had been strongly recommended in France, where large excesses of ethyl alcohol were available. It is also known that the projected production of synthetic rubber in Italy was also being partly based on alcohol (the remainder on acetylene, to fall in line with German practice).

The use of alcohol as material for butadiene during the war expanded the total requirements for industrial alcohol several-fold. Before the war most of the industrial alcohol was produced from molasses, but rapid and great increase in output could be attained only by resort to other materials, principally grain. The increase was obtained chiefly by diverting whisky distilleries to industrial alcohol.

The use of alcohol is no departure from the rule that the fundamental unit in these syntheses is ethylene, for the dehydration of ethyl alcohol gives ethylene:

$$CH_3.CH_2.OH \rightleftharpoons CH_2{=}CH_2 + H_2O$$

Although alcohol is a cheap industrial material, yet in view of the subsequent processing involved it is not cheap enough. Most alcohols are manufactured by fermentation processes based on sugars.

The principal sources are:

1. Starchy materials, such as potatoes, corn, barley, etc.
2. Cane-sugar, molasses, beet-sugar, etc.
3. Wines.

Seen in this light, the raw materials are essentially agricultural and as such, dependent on the vagaries of nature and the food situation.

The processes involved in the production of alcohol are, briefly:

(*a*) The conversion of starchy raw materials into solutions containing sugar;
(*b*) The fermentation and decomposition of the sugars, and
(*c*) The distillation of the alcohols formed.

The position has changed somewhat with improved catalytic methods. The estimate of possible yields of alcohol from the various sources is of great interest.

TABLE 38. YIELD OF ALCOHOL FROM AGRICULTURAL PRODUCTS [22]

Raw material	Alcohol—Gal./acre	Yield—Gal./ton
Sugar Beet	287·0	22·1
Sugar Cane	268·0	15·2
Jerusalem Artichokes	180·0	20·0
Potatoes, White	178·0	22·9
Potatoes, Sweet	141·0	34·2
Apples	140·0	14·4
Raisins	102·0	81·4
Grapes	90·4	15·1
Corn	88·8	84·0
Rice (rough)	65·6	79·5
Molasses (blackstrap)	45·0	70·4
Grain Sorghun	35·5	79·5
Wheat	33·0	85·0

Whenever agricultural surpluses have accrued, it has been suggested to utilize them for the production of synthetic rubber. It has been put forward as an outlet for the enormous over-production of sugar which has been the rule in recent years. The idea of obtaining rubber from potatoes excited great interest at the beginning of the century. Even in this country, when there has been a surplus of potatoes, suggestions

have been made to utilize them for synthetic rubber. Until recently only the Russians had been bold enough to attempt the use of alcohol on a really large scale, starting from potatoes. Moreover they have made the process very efficient for they claim to obtain 600 gallons of alcohol per acre of potatoes. The occasional abundance of corn in some countries has also been a source of interest in this connection.

Activity in the United States has been such that the Baruch Committee recommended the immediate erection of plants to produce 100 million gallons a year on sites near the grain-producing areas. The actual programme far outstrips this. In 1945 in the United States, 637 million gallons alcohol were produced; 282 million from grain, 190 million from molasses and 112 million gallons by syntheses. Of this some 200 million gallons were scheduled for synthetic rubber. Improved accelerated methods of fermentation have latterly been developed which improve the production of alcohol. Thus later methods show a yield of 2·5 gallons per bushel of corn and 2·7 gallons per bushel of wheat.[43]

In actual fact, as demands for grain have become greater, so production has been diverted from agricultural sources to petroleum products.

Much work has been carried out to explore the possibilities of producing synthetic rubber from corn, wheat and other surplus farm crops. Some controversy has arisen as to the merits of making butadiene from alcohol by a number of steps through the aldol process or by a shorter procedure. Thus Standard Oil Co. of N.J. working with aldol estimate to produce 2·2 lbs. butadiene per gallon of alcohol.[40]

On the other hand, Carbon and Carbide Union [5] have a two-step process for the production of butadiene from alcohol. Part of the alcohol for their large butadiene programme is to come from grain. The Szukiewicz process based on alcohol, which involves passing alcohol over a heated catalyst, results in a yield of 75 per cent. butadiene by a single pass (*vide infra*).[38]

Yet another alternative was the proposal to prepare alcohol from waste sulphite liquors from pulp mills, put forward by McCarthy.[20]

A process was developed by Christensen,[6] whereby synthetic rubber can be made from agricultural products. It is claimed that 10 lbs. of synthetic rubber can be obtained from a bushel of wheat, corn, or other agricultural material containing starch or sugar.

The procedure takes the following course:

(i) Preparation of 2,3-butylene glycol by fermentation of sugar or farm crops.

(ii) Evaporation of solution to one-third original volume.

(iii) Glycol is removed by solvent extraction or distillation.

(iv) Conversion of glycol into butadiene by a vapour phase catalytic process.

The process would also yield vinyl compounds from glycol and alcohol, which can also be used to make synthetic rubber. The principal rubber ingredients can be made for 10 cents a pound. The rubber could be produced at 20 cents per lb., and 600,000 tons would involve about 5 per cent. of the U.S. corn crop, or 120 million bushels.

A pilot plant for the production of butadiene from grain by a fermentation process to make butane-diol as intermediate, was built by the Seagram Company. Apparently the procedure is to ferment grain with *Aerobacter aerogenes* for a period of about 40 hours, after which reaction is 90 per cent. complete in conversion to 2,3-butylene glycol. The greatest difficulty lies in separating this from the charge. Butyl alcohol appears to be the best selective solvent for the purpose. The final conversion into butadiene is carried out by forming butylene glycol diacetate which is heated at 500° C. giving a yield of 88 per cent.[13] Yields are between 6·8 and 7·5 lb. butadiene per bushel of corn.

By-products in the manufacture of ethyl alcohol from fermentation spirits include such materials as butyl alcohol, which, of course, can also be used to produce butadiene. Obviously the commercial factors are even greater against this being used as a major source.

Other Agricultural Products. According to Hecht and Reppe,[15] butadiene is produced by leading another agricultural derivative tetrahydrofurane in the gas phase at temperatures between about 250° and 450° C. over a phosphate catalyst having an acid reaction.

The United States Bureau of Agriculture at its Peoria Laboratory of the North-Western University, has made an outstanding development in the production of synthetic rubber-like material from agricultural sources. They have produced a synthetic elastic by the polymerisation of fatty acids obtained mainly from soya bean oil, together with ethylene glycol. The raw materials involved are soya beans, corn, and some vegetable oils. The generic name is Norepol.[33] One commercial type made by the Reichhold Company is known as Agripol.[39]

In general it may be handled just like rubber, the same range of compounding and vulcanizing ingredients being utilized. Similar vulcanizing conditions and times likewise apply. The products do not show such high tensile strength, nor is the resistance to abrasion as good as that of rubber. There appear to be many applications for this material and a quite appreciable tonnage has been produced.

Articles in production include heels, fruit jar rings, tubing, and gaskets. The tensile strength is of the order of 500 lb. per square inch as against 3,000 lb. for rubber, while elongation at 200 per cent. is less than the 600 per cent. elongation of comparable rubber compounds.

Other similar types include: Kempol, Zein, Volitex, Norelac, Witcogum, Aropol, Texalyn.

Synthetic Alcohol as a Possible Source. Apart from new possibilities envisaged by the traditional production of alcohol based on agricultural materials, there appear to be possibilities in the synthetic production of alcohol. The cheap production of ethyl alcohol is a matter of extremely great importance to chemical industries generally. It is estimated that in the United States there is adequate ethylene available to make 1,000 million gallons of alcohol a year.[12]

Ethylene is available in enormous quantities from coke-oven gas, and from petroleum products. Ethyl alcohol can be obtained synthetically from ethylene, reversing the procedure already outlined. Of late there has been a strong trend towards its synthetic production. This has been particularly the case in Great Britain, where activities started as early as 1919. In recent years it has made great strides and is already competitive with ethyl alcohol obtained by fermentation processes. The chief conversion process depends on the fact that ethylene reacts with sulphuric acid to give ethyl hydrogen sulphate, which, when hydrolized, yields ethyl alcohol.

Although this is still the leading synthetic process, new methods are well advanced which in due course may produce much cheaper material. The outstanding trend in this direction is the catalytic hydration of ethylene in the vapour phase under the influence of catalysts, such as sulphuric acid, sulphonated acids, etc., at temperatures of 150°–300° C.

There is a trend for carrying out continuous production of alcohol by treating ethylene with dilute sulphuric acid at high temperature and pressure, which avoids any necessity for reconcentration.

The Standard Oil Company of New Jersey,[40] when expanding their plant at Baton Rouge, La., to produce 10,000 tons of Buna S from petroleum and 5,000 tons of butyl rubber, included as part of the programme the production of 20 million gallons of alcohol.

Synthesis of Butadiene from Alcohol. Once alcohol was available the general method employed was to oxidize this to acetaldehyde. Thereafter this was subjected to aldol condensation. That is to say, under the influence of a small amount of alkali two molecules of acetaldehyde combined to form a new molecule of aldol. This was

one of the earliest known examples of polymerization. The production of butadiene via acetaldehyde is an indirect process requiring a number of stages. Yet it is the basis of German production. The strangest feature of this is that it provides an outstanding example of history repeating itself. The process was first developed by W. H. Perkin, junior, and his associates in 1912. Yet synthetic rubber had the identical frigid reception in Great Britain accorded to synthetic dyestuffs prior to the last war, and which were also subsequently developed by the Germans.

The Russians appear to have achieved some considerable measure of success by a direct method with ethyl alcohol. The production of the chief Soviet type of synthetic rubber, S.K.B., was a direct process based on alcohol obtained from potatoes. The process was developed by Lebedev,[21] and utilized ethyl alcohol, or propyl, or isopropyl alcohols. The method was comparatively simple. The alcohol obtained from potatoes was passed over a mixed dehydration and dehydrogenation catalyst such as alumina and zinc oxide, at a temperature of 400° C. The reaction product was strongly cooled. The uncondensed gas containing most of the butadiene was washed with turpentine or petrol, which removed the butadiene. This was separated and rectified by distillation.

Russian synthetic rubber was made from alcohol at an early date. The Lebedev [27] process was outlined in B.P. 331,482 1930, which claimed :

(1) A method of manufacturing diolefines, consisting of heating methyl, ethyl or propyl alcohol, or mixtures thereof, with a mixture containing a catalyst capable of provoking the splitting-off of hydrogen, and a catalyst capable of provoking the splitting-off of water.
(2) A method of making diolefines, as in claim 1, consisting of the use of reduced pressures and rapid cooling of the products of the reaction.
(3) A method of making butadiene as in claims 1 and 2, consisting of heating ethyl alcohol with a mixture of aluminium oxide and zinc oxide.

The above information was later extended in a Russian patent [26] which mentions that uranium oxide is a catalyst capable of simultaneously splitting off water and hydrogen from alcohols, and that mixtures of hydrosilicates or oxides of aluminium with oxides or salts of manganese, etc., also catalyse the reactions of dehydration and dehydrogenation of alcohols.

The process is based on the overall reaction:

$$2CH_3CH_2OH \rightarrow 2H_2O + H_2 + CH_2{:}CHCH{:}CH_2$$

which should yield:

	Per cent.
Butadiene	58·7
Hydrogen	2·2
Water	39·1

The yield of butadiene was said to be 34 per cent. According to Petrenko [37] there have been considerable improvements in recent years. During 1939 the yield of butadiene from alcohol rose to 36·25 per cent compared with 32·5 per cent. in the previous year. At the end of 1939 the yield was at 41 per cent., representing 70 per cent. of the theoretical. Thus the consumption of alcohol per ton of synthetic rubber decreased from 3·288 tons in 1938 to 2·806 tons in 1939.

Ostromislensky [34] discovered that a mixture of alcohol and acetaldehyde could be made to condense when heated in the presence of a catalyst such as kaolin, with the formation of butadiene. Incidentally, Ostromislensky, in the course of his researches for synthetic rubber, carried out much of the fundamental work which has led up to the commercial application of polyvinyl resins, notably with vinyl chloride.

Lebedev added various substances to the alcohol before contact and investigated their effect on the yield of butadiene.

He confirmed his own earlier conclusions that:

(1) Acetaldehyde takes part in the formation of butadiene, although by itself it forms no butadiene.

(2) Ether takes part in the formation of butadiene, but, unlike acetaldehyde, is capable itself of forming butadiene. However, the yield of butadiene obtained from pure ether is smaller than that from pure alcohol.

(3) Ethylene introduced simultaneously with the alcohol evidently plays a considerable part in the formation of butadiene.

(4) Slight dilution with water has practically no effect on the yield of butadiene. At greater dilution, the yield falls off rapidly.

In practice, crude alcohol (84·6 per cent. absolute alcohol by weight) is used, and this gives a yield of butadiene equal to that of rectified alcohol (92·5 per cent. absolute alcohol by weight). According to Sabatier, water is detrimental to the dehydrogenating process. This was confirmed by Lebedev's collaborators, who obtained the following yields, when all other conditions were kept constant

TABLE 39

Percentage of volume of absolute alcohol in the alcohol used	Temperature (° C.)	Percentage yield of butadiene (calculated on absolute alcohol consumed)
94·5	440	23·2
94·5	500	17·7
76	440	16·5
76	500	19·3
54	440	15·0
54	500	18·8

A slight improvement is observed when the more dilute alcohol is contacted at higher temperatures.

(5) Butyl alcohol takes no part in the formation of butadiene, and its presence impairs seriously the yield of butadiene.

Bearing in mind these Russian developments it is interesting to consider the United States activities in closer detail. The leading method practised by the Carbide and Carbon Union made butadiene

BUTADIENE FLOW CHART

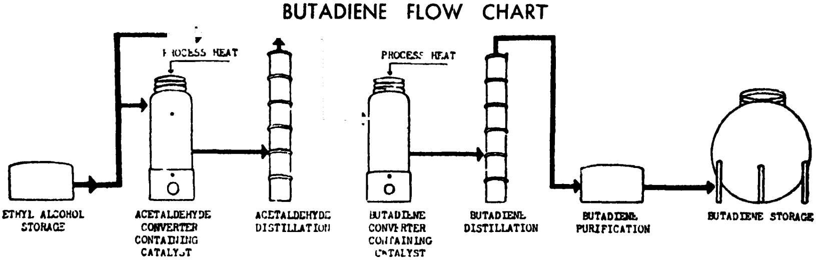


FIG. 12.

on the largest possible scale from alcohol and acetaldehyde, i.e. from alcohol. Most of the alcohol used comes from grain, etc., by improved fermentation processes.

At the present time, 240,000 tons of synthetic rubber per year is scheduled for production based on butadiene from alcohol. The major portion of this is being made by the Carbon and Carbide Union, based on alcohol, chiefly derived from corn and wheat. This company is also using synthetic alcohol. They have a very successful process, and have led the way in getting into production.

The other alcohol process of interest in the United States was known as the Publicker Process, developed by Szukiewicz. He had built plants in Poland and in Italy before the war. At first the value of his process was underestimated. Investigation proved it to be at least as effective as any other. Superficially it appeared to have a number of

features in common with the Carbon and Carbide process; closer examination shows this is not the case.

The Carbon and Carbide Process.[4] Alcohol and acetaldehyde are catalytically converted into butadiene. This is separated from the by-products and unchanged alcohol and acetaldehyde, which are re-used. The converters consist of 753 steel tubes, 20 ft. long by 3 in. diameter, containing catalyst. The tubes are surrounded by a tempera-

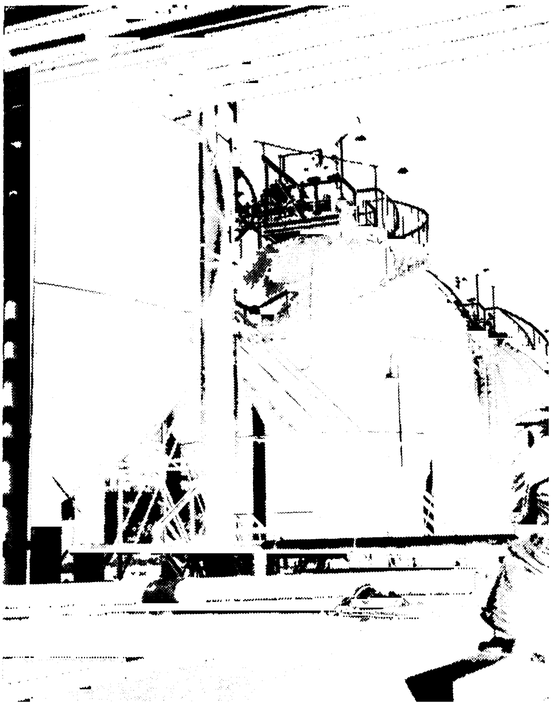


FIG. 13.—Storage Tanks for Butadiene.

ture regulating bath of "Dowtherm" liquid. A 20,000-ton unit possesses 12 such converters, 4 converting alcohol to acetaldehyde by means of one catalyst, and 8 making the butadiene with another catalyst. So that it is a two-stage process. The yield is about 2·3 lb. of butadiene per gallon of 95 per cent. alcohol. The catalyst becomes foul after a time, and is cleaned by passing air over to burn off the carbon. During a single passage, about 10 lb. of the alcohol mixture has to be vaporized to give 1 lb. of butadiene, the remainder being re-cycled and used again. The butadiene is obtained 97 per cent. pure.

The Publicker Process.[38] In this case alcohol alone is employed. It is vaporized and passed over a catalyst at about 400° C., being converted substantially into butadiene. The butadiene has to be separated from the other reaction products. The set-up resembles that for the previous process, i.e. there are many tubes, this time 10 feet long by 1½ inches diameter. They are heated by molten salt. The catalyst is in due course poisoned by the deposit of carbon which is then burnt off with a stream of air and the catalyst regenerated. The catalyst is a uranium salt.

An advantage of the process is that alcohol is converted into butadiene in a single stage, the conversion reaching 75 per cent. The yield of butadiene is 2·3 lb. per gallon of 95 per cent. ethyl alcohol with the prospect of reaching 2·5 lb. per gallon.

The by-products, apart from butadiene, contain mainly ethylene, butylene and water. The butadiene is obtained at 80 per cent. purity, and is comparatively easily purified up to the specified 99·5 per cent. It is of interest that the ethylene produced is more than adequate for use in the production of the requisite amount of ethyl benzene for the styrene involved in the conversion of the butadiene to Buna S. The comparison of the two processes is outlined in Table 40.

TABLE 40. COMPARISON OF ALCOHOL PROCESSES[43]

	Carbide and Carbon	Publicker
(*a*) Alcohol converted to acetaldehyde	50 per cent.	None
(*b*) Pounds vaporisation of charge per lb.—butadiene	10	5
(*c*) Pounds condensation for re-use per lb.—butadiene	8	1½
CONVERTER		
(*d*) Tube Material	Steel	Steel
(*e*) Inside diameter of tube	3 inches	1½ inches
(*f*) Heating method	" Dowtherm "	Molten Salt
(*g*) Reaction Temperature	315 deg. C.	405 deg. C.
CYCLE		
(*h*) On Stream	6 days	4 hours
(*i*) Regeneration of Catalyst	1 day	2 hours
(*j*) Per cent. time on Stream	85·5 per cent.	66·7 per cent.
PRODUCTION		
(*k*) Lbs. butadiene per hour per lb. Catalyst	On Stream 1·5 Average hour 1·3	3·6 2·4
(*l*) Yield—lbs. pure butadiene per gallon alcohol (100 per cent. at 20 deg. C.)	2·3–2·4	2·1–2·2
(*m*) Purity of crude butadiene	97 per cent.	80 per cent.

Considering both these processes from the engineering point of view on a large scale, it is clear that the vaporization of alcohol is not a difficult operation, nor is the passage over a catalyst. This contrasts with the complex high pressure arrangements involved in the case of the petroleum derivatives, and also the somewhat involved chemical syntheses working from carbide. Of course, the butadiene in all the processes must be collected, separated and purified. Butadiene for making GR-S (Buna S) must be 98·5 per cent pure.

It is interesting to compare the American experience from the point of view of construction materials. The following Table summarizes the known facts.

TABLE 41. CONSTRUCTION MATERIALS, ETC., INVOLVFD PER 1,000 TONS BUTADIENE [38]

Process	Steel	Copper	Chrome	Nickel	Compressor Capacity Horse Power
	Tons	Tons	Tons	Tons	
Petroleum (Butane) . . .	165	9·0	5·0	2	
Petroleum (other Processes) .	194	—	—	—	312–490 H.P.
Alcohol (Carbon and Carbide)	140	50·6	2·2	1	180 H.P.
Alcohol (Publicker) . . .	100	10	0·1	—	100 H.P.

Acetylene—An Established Source of Synthetic Rubber. At the present time one of the chief sources of butadiene, chloroprene, ethenoid resins, etc., is undoubtedly acetylene obtained from calcium carbide. Acetylene is also obtained in large quantities from coal hydrogenation, petroleum wastes, etc. Acetylene can be obtained by the pyrolysis of methane, of which, throughout the world something like 10 million tons a year is available.

Carbide is one of the most important industrial chemical raw materials steadily increasing in importance. For many years the Germans have concentrated on the use of carbide as a source of numerous chemicals, notably acetaldehyde, acetic acid, and numerous other derivatives. Reppe in particular has been responsible for many outstanding developments in this field. It is one of the mainstays of their chemical industry. It is certainly the backbone of their synthetic rubber industry and their plastics industry. Prior to the war they were consuming 600,000 tons per year. We normally import about 60,000 tons per year. At the peak of their synthetic rubber production, output far exceeded this, being 1,320,000 tons per annum.

Among leading important industrial materials obtained from acetylene are:

Acetic acid, which is important for so many chemical industries including rayon, plastics, dyestuffs, explosives, etc.;

Ethyl alcohol, which is necessary as a solvent for dyestuffs, chemicals, explosives, motor fuel, etc.;

Acetone, which is essential for explosives, for lacquers, and innumerable chemical processes;

Ethyl acetate, which is a leading solvent;

Trichlorethylene; and a host of other synthetic chemicals, plasticizes, solvents, etc.

It is the parent material of numerous plastics, including the leading ethenoid resins such as polyvinyl chloride, polyvinyl acetate, etc. It is a source of vinylacetylene from which chloroprene is made, and other polymers which have attained commercial significance. It is also the source of acetylene black, one of the leading filling materials in a number of industries, including rubber.

The importance of the carbide industry to plastics and industry in general has often been stressed.

The importance of carbide and therefore coal as a source material has never been fully appreciated in Great Britain. Some indication of the significance may be gained from Fig. 16.

The Schkopau Works.[45] The range of products made by the I.G. Farbenindustrie A.G. Bunawerke at Schkopau forms a typical example of the work carried out on the basis of acetylene. It is interesting to consider this plant, which represented the largest synthetic rubber plant in Germany, with a rated capacity of 6,000 tons per month, and was also a plant primarily concerned with maximum production.

Construction of the plant was started in 1937, and the plant began to operate in bulk capacity in 1939. Additional units were added from time to time and when occupied by the Allies some 11,205 men were being employed. Of this number approximately 3,075 were used on production units, 1,760 were employed in the sections producing synthetic rubber and its intermediates, the remainder being employed in the miscellaneous sections and in a somewhat unusually large force of constructors. The plant covered an area of approximately 1½ square miles.

Steam was produced in six high-pressure boilers at 110 atmospheres. Five boilers were operated, with one spare unit, each having a capacity of 800 tons of steam per hour. The boilers were operated from seven to eight months before cleaning, each boiler working on the average ten months each year. Electricity required was generated in 18,000-kW.

generators, two generators being driven by one steam turbine placed between. Steam entered at the generating pressure of 110 atmospheres, and passed as exhaust from the first turbine at 15 to 16 atmospheres, part of the steam going to the factory as the plant high-pressure steam supply. The rest of the steam passed to the second turbine, from which it was exhausted at 4 atmospheres pressure. By the use of a heat exchanger, this exhaust steam was used to generate factory low-pressure steam at $2\frac{1}{2}$ atmospheres, for which there was a heavy demand. The steam consumption of the generators, when operating at 18,000-kilowatt load, was 5·4 kg. per kilowatt and from 5·6 to 5·7 kg. per kilowatt if required to operate at a load of 20,000 kilowatts.

FIG. 14.—The carbide plant at Schkopau.

The plant was a large consumer of electrical power chiefly for the carbide furnaces which at full capacity required 176,000 kilowatts. A further 15,000 kilowatts was used in the chlorine plant, the rest of the plant taking 50,000 kilowatts. Additional power was obtained as required from other I.G. plants in the district.

Products Manufactured. Although primarily concerned with the manufacture of Buna S3, the numbered Bunas 32 and 85 and their intermediate products, the plant also produced a number of other chemicals, chiefly derived from acetylene. The factory, for example, was stated to produce from 70 to 80 per cent. of the vinyl chloride made in Germany and, in addition, acetic acid and ethylene oxide. Phthalic anhydride, trichlorethylene, formaldehyde, etc., were also produced,

and polystyrene in addition to the styrene required for the manufacture of Buna S3.

A list of the main products produced is given in Table 43. Against each item is shown the estimated plant capacity. In addition to these major items of production, products such as Nekal BX (sodium dibutyl naphthalene sulphonate), the emulsifier used for the polymerization of Buna S, and aluminium chloride for the manufacture of ethyl benzene, were also made domestically. Nekal was made from butanol, naphthalene, sulphuric acid and oleum, in a plant with a capacity of 300 tons per month. Aluminium chloride was produced from phosgene and bauxite, the phosgene in turn being produced from carbon monoxide made from oxygen and coke, a very pure carbon monoxide being required.

Schkopau was, therefore, largely a self-contained plant capable of producing a very wide range of materials essentially based on carbide

TABLE 42. INTAKE OF RAW MATERIALS AT SCHKOPAU

Material	Amount required per month	Source (where indicated)
Brown coal	180,000 tons	Geisel (nr. Merseberg) Waldenburg (Silesia)
Coke or anthracite	10,000 ,,	Ruhr district
Burnt chalk	10,000 ,,	Harz district
Hydrogen	5,000 cu. m. per hr.	Leuna
Benzene (refined)	1,000 tons	Arbo (Bochum)
Tar	1,500 ,,	Leuna or I.G. Bergwerke
Naphthalene	85 ,,	Essen

Also rock salt, methanol, and bauxite.

manufacture. Although interlinked in some ways with other chemical industries in the district, as will be seen by comparing Table 42 which gives a list of the main raw materials entering the plant, with Table 43, which covers the main products made, the plant was essentially based on the conversion of primary raw materials into a very wide range of important and, to a large extent, nationally essential chemical products.

The Manufacture of Calcium Carbide. The commercial manufacture of calcium carbide was started towards the end of the last century, and is now the largest consumer of energy in the electric furnace industry. The chief considerations in establishing a carbide factory are supplies of raw material which consist of limestone and coke or anthracite, and an abundant supply of cheap electric power. The latter item contributes the chief cost factor. It is found that many large carbide factories have been set up on sites where cheap hydroelectric power is available. The preparation of raw materials is a matter of some importance owing to the high temperatures involved.

TABLE 43. PRODUCTS MADE AT SCHKOPAU AND CAPACITIES

Material	Capacity per month
End Products:	
Buna S	6,000 tons
Buna 32	200 ,,
Buna 85	100 ,,
Vinyl chloride	2,900 ,,
Polyvinyl chloride	600 ,,
Polystyrene	50 ,,
Ethyl alcohol	800 ,,
Butanol	500 ,,
Acetic acid	700 ,,
Acetone	200 ,,
Phthalic acid	540 ,,
Formaldehyde (100 per cent.)	800 ,,
Diglycol	700 ,,
SS oil (lubricating oil)	500 ,,
Tetrahydrofurane	300 ,,
Trichloroethylene	400 ,,
Ethyl chloride	120 ,,
Waste lime (used for manure)	14,000 ,,
Caustic soda lye (NaOH)	4,500 ,,
Aluminium chloride	700 ,,
Intermediate Products:	
Ethyl benzene	1,800 ,,
Styrene	1,600 ,,
Calcium carbide	30,000 ,,
Acetylene	10,000 ,,
Acetaldehyde	12,000 ,,
Aldol	11,000 ,,
Butylene glycol	10,000 ,,
Butadiene	4,800 ,,
Chlorine	4,000 ,,

Limestone, which is calcium carbonate, is heated at a very high temperature in lime-kilns to drive off carbon dioxide. The present-day practice employs lumps of lime reduced to pieces from 1 to 2 inches in size, while coal is reduced to pieces between $\frac{1}{4}$ and $\frac{1}{2}$ inch mesh. The ingredients are mixed in proportions of about 100 parts of lime to 65 parts coal. The electric furnaces used are of special construction and have to withstand temperatures up to 3,000° C. Enormous electrodes are employed, ranging up to sizes of about 22 inches square. It is said that the progress in the design of electric furnaces for high temperatures follows developments in carbide manufacture.

As a result, manufacturing plants are chiefly located where there is unlimited water power. Norway and Sweden have been the chief European producers, although requiring to import coal. Until the war Great Britain was almost the only industrial country without a carbide industry, although possessing all the conditions necessary. The advances in the production of thermoplastics have largely come about

because of this extensive manufacture. Correspondingly, the absence of such activity has led to neglect of the newer plastics, as in Britain.

In 1942 German carbide capacity was 1,320,000 tons per annum. Something over half this quantity was applied to "acetylene chemistry".

The actual production of carbide involves heating a mixture of lime and coal in electric furnaces by means of the electric arc. Extremely high currents are passed through built-up electrodes, Söderberg continuous electrodes appear to be generally used now in all parts of the world. This is a light steel casing containing a carbon paste. This is fed continuously into the furnace at the rate of 40 cm. per 24 hours. One typical modern plant, for example, using 23,000 kilowatts and a single three-phase supply three-phase 50 cycles with 180 volts across electrodes. The temperature reaches 3,000° C., when a fluid melt of carbide is formed and may be tapped off. The batch size is of the order of four tons in the most efficient plant, the furnace being continually fed with fresh materials. The largest commercial units produce about 200 tons per day. One ton of carbide requires 3,300 units of current for its manufacture, including the amount required for crushing, grinding, and all other processes. German experience was that the most economical unit was about 25,000 tons per annum.

Large capacity carbide plants are features of the enormous German synthetic rubber-manufacturing units.

The following account by Ambros [2] of the process carried out at the enormous Schkopau Buna Works gives some idea of the principles adopted. This plant alone produced almost 300,000 tons per annum.

Acetylene Production. Carbide is manufactured at a large carbide works. The notable things about this factory, which has the most modern carbide furnace in the world, includes the amazing freedom from dust, which is carried away by a very comprehensive and efficient equipment. Another noticeable feature is the great extent to which mechanizing and automatic control of the various furnace processes has been carried. The furnaces are fitted with external instruments which control all measuring, mixing, and regulating equipment, all of which are simultaneously co-ordinated, being supervised by specially skilled operatives. For example, the movement of the electrodes, the addition of coke and lime, etc., are all adjusted by these external controls. The mighty furnaces work continuously, the power being obtained from mid-German brown coal; the resulting carbide comes to the ovens as a molten white fluid, and enters a sealed water-cooled inclined conveyor, on which it cools down, and in so doing breaks into small pieces, so that at the end of the run cooled and crushed carbide is obtained.

This carbide is ground to powder in a separate mill, and then goes to the gassing chamber, which works so that gassing is carried out without the formation of sludge, as a result of which dry, finely-powdered lime remains. This gassing chamber is also fully mechanized, being operated by a few skilled men with the help of centralized controls. The remaining spent lime is

partly used for agricultural purposes, while part is regenerated by burning and is used once again in the furnace. In this manner it has become possible to utilize a considerable portion of reclaimed lime in the manufacturing process.

The major production is, of course, butadiene, for synthetic rubber. Acetylene is obtained from carbide by addition of water. For the manufacture of butadiene the next step is to produce acetaldehyde. The manufacture of acetaldehyde from acetylene is carried out by passing acetylene into a dilute sulphuric acid solution containing a catalyst generally composed of mercury salts. This is one of the fundamental reactions of industrial chemistry. This is the basis of the major portion of Germany's large-scale production of Buna synthetic rubbers.

The Electric Arc Process.[44] Apart from the carbide process, the Germans produced about 5,000 tons per month of acetylene by the electric arc process at Huls. There were three sources of raw material:

(*a*) Natural gas, mainly composed of methane.

(*b*) Coke-oven gas which had passed through a deep refrigeration system—the Linde process.

(*c*) Refinery gases.

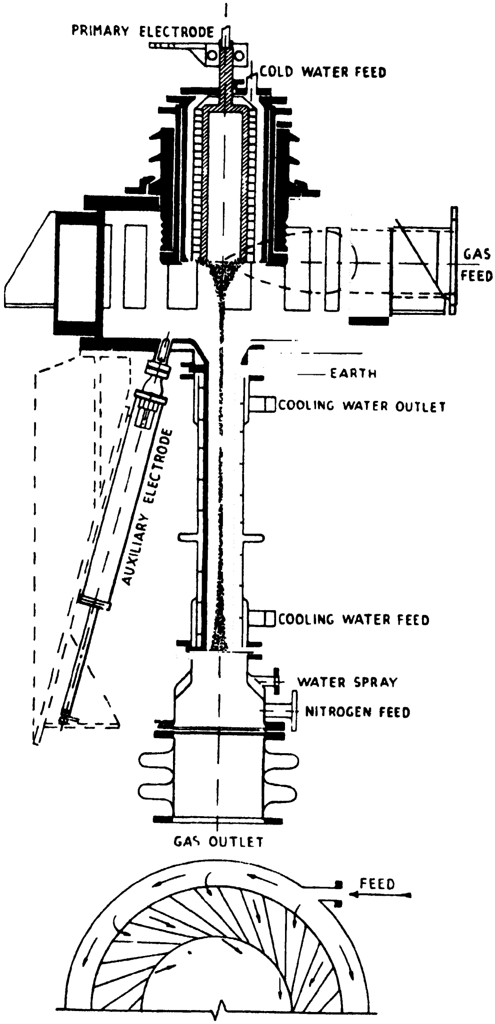


FIG. 15.—Electric Arc Method for making Acetylene.

The gas is passed into an electric arc formed by 6,000-volt A.C. 50-cycle

current converted in a mercury rectifier to 7,000 volts D.C. at 7,000 kilowatts. Each arc uses 7,000 kilowatts and produces 4,200 cubic metres per hour product. Power consumption is about 4 kwh. per lb. crude acetylene and about 5 kwh. per lb. pure acetylene.

The plant contained fifteen sets of arcs. Each set consisted of one mercury arc rectifier for converting alternating to direct current and two arc-reaction tube units. Only one of these, however, was on stream at any time, the other being held as a standby.

The arc operated at 1·5 atmospheres, 1,000-volt direct current, a reaction tube terminal temperature of 1,600° C. being reached; 7,000 kilowatts were required for a gas input of 2,800 cubic metres per hour. The conversion per pass was 50 per cent. and the ultimate yield was acetylene 45 per cent., carbon black 5 to 6 per cent., and from 2 to 10 per cent. of ethylene, depending on conditions. The production per arc was approximately 15 tons of acetylene a day.

The arc reaction tube unit used is shown in the figure. The high voltage lead to the primary electrode, which was made of copper, entered at the top. The electrode was jacketed for water-cooling and insulated with porcelain.

The feed gases entered tangentially, circulating round in a circular space in the expanded head section and passed through vertical slots to the arc zone at the centre and then down to the reaction tube. This produced a high velocity swirling action and so prevented the electrode burning out or carbon disposition. The second electrode consisted of a copper gasket at the head of the reaction tube, and was earthed. An auxiliary electrode was used for starting up.

After quenching the exit gas from the reaction tube to 150° C. (dew-point 92°), it was then passed through two cyclones in which from 60 to 70 per cent. of the total carbon black present was deposited. The gas was sprayed with water in a wash tower and passed through bag filters to remove the residual black, the bags being heated to prevent condensation. The gas was then sprayed with water at 20 to 25° C. to bring the temperature of the gas below the dew-point and so deposit most of the water carried in the gas.

After removing the higher boiling constituents by counter-current washing in an aliphatic oil, the gas was compressed to 19 atmospheres and absorbed in water in perforated plate towers. The acetylene was then stripped from the water by four stage flushings to a final pressure of 0·05 atmospheres absolute.

The gas obtained from the first stage was too low in acetylene (45 per cent.), and this was therefore recompressed and recycled through the absorber. The gas from the second, third, and fourth flushes, however,

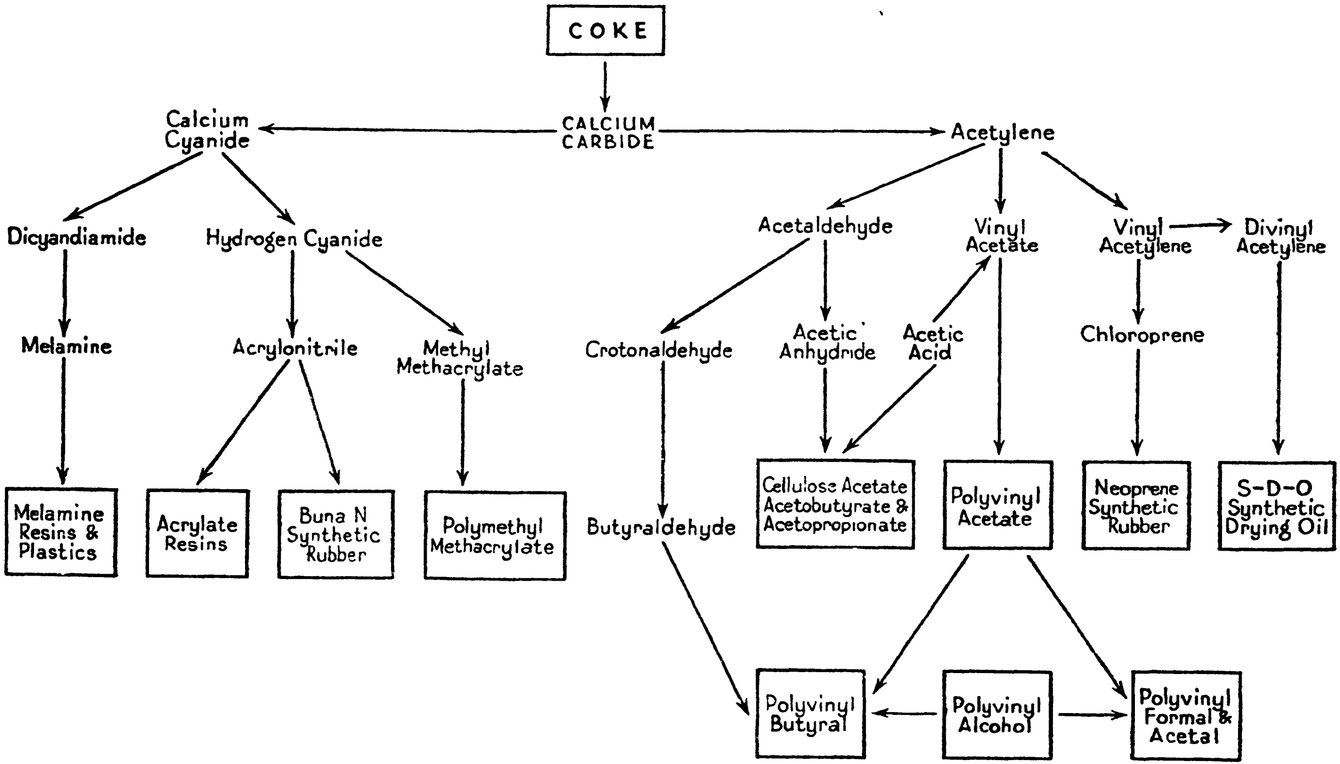

COKE
CALCIUM CARBIDE
Calcium Cyanide
Acetylene
Dicyandiamide
Hydrogen Cyanide
Acetaldehyde
Vinyl Acetate
Vinyl Acetylene
Divinyl Acetylene
Melamine
Acrylonitrile
Methyl Methacrylate
Crotonaldehyde
Acetic Anhydride
Acetic Acid
Chloroprene
Butyraldehyde
Melamine Resins & Plastics
Acrylate Resins
Buna N Synthetic Rubber
Polymethyl Methacrylate
Cellulose Acetate Acetobutyrate & Acetopropionate
Polyvinyl Acetate
Neoprene Synthetic Rubber
S-D-O Synthetic Drying Oil
Polyvinyl Butyral
Polyvinyl Alcohol
Polyvinyl Formal & Acetal

FIG. 16.

was brought together as crude acetylene of 90 per cent. purity. It was brought up to 97 per cent. concentration by (i) low-temperature condensation and evaporation, using liquid ammonia, and (ii) scrubbing with a petroleum distillate which removed the higher acetylenes. Carbon dioxide was then removed by scrubbing with caustic soda solution to give a final purity of 97 to 98 per cent.

Oxidation of acetaldehyde yields acetic acid. Vinyl acetate is made by passing acetylene into a solution of acetic acid containing catalysts.

Butadiene from Acetylene. Acetylene is obtained from carbide by addition of water. For the manufacture of butadiene the next step is to produce acetaldehyde. The manufacture of acetaldehyde from acetylene is carried out by passing acetylene into a dilute sulphuric acid solution containing a catalyst generally composed of mercury salts. This is one of the fundamental reactions of industrial chemistry. It appears that this is the basis of the major portion of Germany's large-scale production of Buna synthetic rubbers.

When starting either from alcohol or from acetylene it is quite evident that acetaldehyde is the real starting point in the production of butadiene. There seems little doubt that in the weighing up of the respective merits of these raw materials, carbide is far cheaper. In fact, acetylene has been seriously considered as a source of alcohol. At any rate, the use of carbide has expanded even in the U.S.S.R.

$$\underset{2{\cdot}1\ \text{tons}}{CaC_2+H_2O} \longrightarrow CH\ \ CH + CaO$$

$$\underset{\text{Acetylene}}{CH\ \ CH} \xrightarrow[\text{solution}]{\text{catalyst}} \underset{\substack{\text{Acetaldehyde}\\ 1\ \text{ton}}}{CH_3.CHO}$$

$$CH_3.CHO+CH_3.CHO \xrightarrow[\text{alkali}]{\text{dilute}} \underset{\text{Aldol}}{CH_3.CH(OH).CH_2.CHO}$$

$$CH_3.CH(OH).CH_2.CHO \xrightarrow{\text{reduce}} \underset{\text{Butylene glycol (almost 100\%)}}{CH_3.CH(OH).CH_2.CH_2OH}$$

$$CH_3.CH(OH).CH_2.CH_2OH \xrightarrow{\text{dehydrate}} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

FIG. 17.—Aldol Synthesis.

According to Frölich and Morrell, the dehydrogenation of ethyl alcohol to acetaldehyde proceeds smoothly in the vapour phase with the aid of a suitable catalyst, which may be of the copper-zinc oxide type, at temperatures of 200° to 350° C. When recycling of uncon-

verted alcohol is employed, a yield in excess of 90 per cent. may be obtained on a mol basis.

The conversion of acetaldehyde to aldol may be carried out at temperatures around 0° C. in the presence of dilute alkali. When properly controlled, this reaction may also be carried to about a 90 per cent. yield. The aldol is quite easily hydrogenated in aqueous solution at 80° to 90° C. under hydrogen pressure of 1,500 to 3,000 lb./sq. in. With a nickel or copper catalyst, yields of 85 per cent. can be obtained.

The last step, involving the dehydration of the 1,3-butylene glycol, is the most difficult of the four reactions. Of the many catalysts which have been suggested, those composed of phosphates and sulphonic acids appear most promising. The indicated yield is of the order of 90 per cent. for operation at temperatures below 400° C.

Thus an overall yield of butadiene on alcohol of about 60 per cent. may possibly be realized by this four-step process. However, as similar yields can be obtained from alcohol by a more direct method, the aldol condensation has found its main application when acetylene is the starting material. In that case, the first step consists of hydrating the acetylene to acetaldehyde:

$$C_2H_2 + H_2O \rightarrow \text{Acetaldehyde}$$

This reaction is carried out in the liquid phase using a mercury salt as the catalyst.

Another method for making butadiene involves the direct union of acetylene and ethylene at 50 atmospheres pressure and 500° C. in tubes containing alkali metal oxides.

Butadiene from Acetylene in Germany.[45] Detailed information is now available concerning the German production of butadiene from acetylene.

Acetaldehyde Production. Acetylene is converted to acetaldehyde in rubber-lined towers, acetylene and sulphuric acid going into the base of the tower. The catalyst used is mercuric sulphate and iron sulphate solution.

At Schkopau there are two acetaldehyde plants—one containing 8 reacting units turning out 40 tons per day, and the other plant with much larger reactors where 4 units make 60 tons per day. No acetaldehyde is stored at the producing plant but goes through pipe lines as produced immediately to the underground storage tanks behind the aldol plant.

The conversion for each passage of acetylene was about 55 per cent. Final yield is from 93 to 95 per cent. of theory. Acetaldehyde is obtained at 99·9 per cent. purity.

Aldol. Six aldol units need be operated to produce the required output of 60,000 tons per year. Each aldol unit is made up of a series of horizontal pipes connected with each other like an S-bend type cooler. The acetaldehyde-aldol solution is circulated. The pipes are about 10 to 12 inches in diameter, made of steel, and a number of the sections consist of cooling units. These are of tubular construction, aldol passing through the tubes with water on the outside. The reaction is carried on at 20° C. If the temperature goes higher, homologues of aldol (6 to 8 carbon atom products) are formed.

Caustic potash solution is used as catalyst (about 1·3 per cent. KOH by weight in the form of a 10–11 per cent. solution in water) on the acetaldehyde.

The aldolization is carried to about 50 to 51 per cent. aldol, 49 to 50 per cent. acetaldehyde, and the stream of material from the pipe reactor is neutralized with phosphoric acid to a mixture of K_2HPO_4 and KH_2PO_4. The crystals are allowed to settle, then centrifuged. The acetaldehyde is then stripped from the crude aldol in an aluminium column using live steam. The aldol-acetaldehyde solution passes through an ingenious system of four-pass heaters. In this way the liquid is stripped from acetaldehyde.

The liquid from the bottom of the stripping column has the following approximated composition :

	Per cent.
Aldol	75
Acetaldehyde	5–10
Water	20
Crotonaldehyde	1
Residue	1–2

Butol. Aldol is reduced to butol (or butylene glycol) by hydrogen gas in six high-pressure reactors. These reactors are 800 mm. diameter, 18 metres long, and of steel construction. The catalyst is a copper chromium oxide catalyst or broken pieces of silica gel, 1 to 4 mm. in diameter. The catalyst is stated to contain 18 to 20 per cent. of copper, 1·8 per cent. of chromium oxide. Hydrogen under high pressure is passed through.

The temperature of hydrogenation is 60° to 65° C. at the start with a new catalyst charge. Pressure is nearly 300 atmospheres. The temperature at the end of the useful catalyst life goes up 80°–85° C. as the activity of the catalyst declines. The yield of by-product butanol at the beginning with a new catalyst is only 3 to 4 per cent., while towards the end of the catalyst life 6 to 10 per cent. butanol is formed.

The butylene glycol reaction product goes to fractionating columns.

In the first column all the low-boiling products are taken off—acetaldehyde, alcohol, butanol, and some of the water. The temperature at the top of the column is 80° C. The rest of the water, the butol, and other high-boiling materials, pass from the bottom of the column. Ethyl alcohol and butanol are taken off from the next column.

FIG. 18—Fractionating columns at the Buna works.

Conversion of Butol to Butadiene. The vacuum-distilled butol (butylene glycol) is 99 per cent. pure as delivered. It is first vaporized at its boiling-point, 210° C., and mixed in equal parts with superheated steam at 450° C. The temperature of the resulting mixture is 270° C., which is the desired temperature in the reactors Each reactor is 2·7 metres in diameter by 5 metres high, the volume is about 16 cubic metres. The catalyst consists of sodium acid pyro-phosphate ($Na_2H_2P_2O_7$) with traces of H_3PO_4 deposited on 10-mm. diameter

pieces of coke. The reactors are heated with internal pancake coils, using 70 atmosphere steam (285° C.) inside the coil. The coils are set 27 cm. apart. It is very important to maintain the temperature as close as possible to 270° C.

The yield of butadiene is 80 per cent. of theory; 3 per cent. of propylene is also formed and 1 to 1½ per cent. butylene-1 and butylene-2. There is also a mixture of partially reduced materials which cannot be recycled, croton alcohol, butyraldehyde, etc. In addition there are also by-product materials consisting of 4-carbon, 6-carbon and 8-carbon alcohols, and also higher condensation products. The various products formed in relation to butadiene are:

80	parts butadiene
3	parts propylene
1	part butylene
3	parts croton alcohol
3	parts butyraldehyde
90	total

Plus 3 to 4 parts of oils.

The gas is scrubbed with 30 per cent. caustic potash (KOH) to resinify traces of aldehyde. The resins formed with caustic potash are liquid and can be readily separated. For 100 parts of butadiene one part of residue is formed. The gas then goes to the compressor, where it is compressed to 5–6 atmospheres and is condensed by water cooling.

The crude butadiene now contains only 0·001 per cent. of water and 0·001 per cent. of aldehyde. A low water content is very important for the numbered Bunas and a low aldehyde content is considered important for all uses since aldehyde is considered a "carrier" for oxidation to the undesirable and dangerous butadiene peroxide. Purification of butadiene is carried out at atmospheric pressure. The gas first goes to a depropanizer, a thirty-plate tin-lined tower where the gas enters at the twelfth plate from the bottom. The propylene at − 45° C. (the boiling-point at atmospheric pressure) goes overhead through a heat exchanger to a compressor where it is compressed to 6·1 atmosphere pressure. The compressed gas is sent to a heater in the bottom of the column where the condensed propylene forms the heating source for boiling the butadiene and the column bottoms. The liquefied propylene from the heater goes to a receiver where seven parts are returned to the top of the column as reflux and one part goes forward and is cooled through the heat exchanger.

The purity of propylene is stated to be 99·85 per cent. 0·1 per cent. propylene remains in the butadiene coming off the bottom of the

column. The bottom material goes to another thirty-plate column (all columns are tin lined), 1·6 cubic metres in diameter, entering at the ninth plate from the bottom. This column also operates at atmospheric pressure. The overhead is condensed with refrigerated brine kept at a temperature of − 20° C. Very little reflux is used—ratio 0·2 to 1. The butadiene purity runs about 99·3 per cent.

Most of the butol produced at Schkopau is used for making butadiene. Ten thousand tons per month was the rated production capacity. Fifty to 100 tons of butol per month are sent to other I.G.

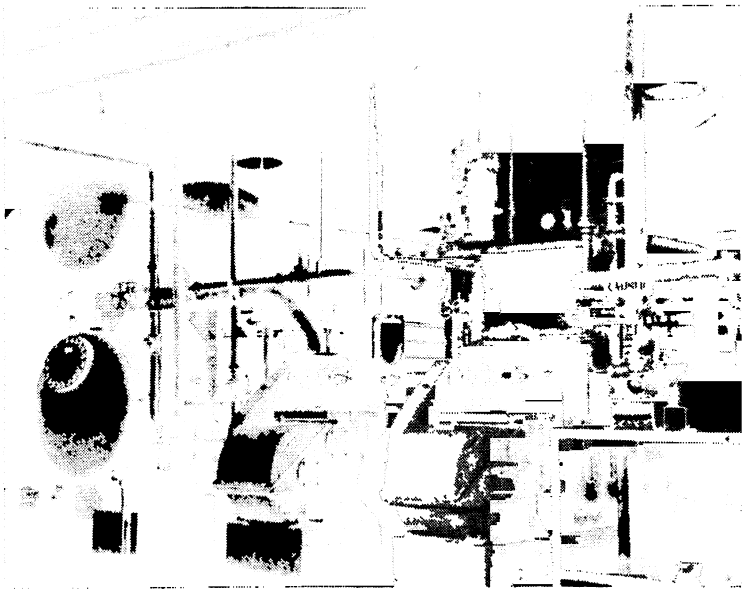


FIG. 19.—Butadiene Purification Unit. When butadiene comes in tank cars inhibitors are added to keep it from polymerizing. Inhibitors are taken out in this process.

works, where some was used for making resins with phthalic anhydride. The balance of the butol is used to make butadiene at Schkopau. By-product propylene is sold for use as a compressed gas.

The highest butadiene production turned out at Schkopau was 4,950 tons in 30 days. Two hundred and eight parts of butol are consumed per 100 parts of butadiene turned out. No inhibitor is used in the storage of butadiene.

United States Interest in Carbide. The United States is a large producer of calcium carbide. As a result, the firms concerned have played a leading part in developing thermo-plastics of the vinyl type,

for example, the Carbide and Carbon Corporation, specializing in carbide production, was responsible for the first large-scale commercial production of polyvinyl chloride and its copolymers in the form of Vinylite products. In a similar manner Shawinigan Corporation in Canada has been largely responsible for the development of products such as vinyl acetates, alcohols, formals, acetals, etc.

B. F. Goodrich Co. have a very large plant at Niagara where the raw material for Geon (polyvinyl chloride) is prepared.

It is interesting to note that the United States firms would not launch out into synthetic rubber production on an acetylene basis. With all their resources of lime and coal and unlimited cheap electrical power, they held back. There is much evidence to show that they were nevertheless extremely interested in the possibility, being cautious merely because of the developments with petroleum products which they knew lay ahead.

Many other methods have been devised for making butadiene from acetylene. When acetylene is passed into dilute solution of cuprous chloride monovinylacetylene is formed. Thus Leuhdeman, Reppe and Rothhaas [29] continuously converted monovinylacetylene into butadiene by bringing it into contact with an aqueous solution of an alkali metal by dioxide and zinc dust, these being added continuously as they are used up. The butadiene formed is continuously removed. Acheman, Lehrer and Stadler [1] treated vinyl acetylene with amalgams of alkali metals in the presence of water or an alcohol which develops hydrogen.

According to Hurukawa,[20] acetylene bubbled into aqueous copper chloride-ammonium chloride mixture gave about 20 per cent. conversion of acetylene, and production of 73 per cent. by weight of monovinylacetylene. Ethyl acetate or acetone solution of monovinylacetylene hydrogenated with palladium black or palladium-kieselguhr gave about 60 per cent. yield of butadiene. Zinc and alkali as reducing agent gave over 95 per cent. yield of pure butadiene. The small amount of monovinylacetylene remaining in the butadiene can be completely removed by sodium or sodamide.

Another German method for obtaining butadiene from butylene glycol is as follows: [8]

Water is split off from 1 : 3-butylene glycol by means of dehydrating catalysts such as sulphuric acid, acid salts of sulphuric acid, sulphonic acids, phosphoric acid, and so on, in the presence of a large amount of water. For example, 80 parts of the glycol dissolved in 20 parts of water was passed at a rate of about 800 parts per hour into 2,000 parts of 1 per cent. sulphuric acid boiling at about 200° C. in an autoclave, the butadiene formed being withdrawn as fast as it is formed. The

water produced by the splitting is drawn off with the help of a separator, and the process can proceed for indefinitely lengthy periods.

According to the I.G.[21] butadiene can be obtained in good yields from normal butylenes by leading them in admixture with at least an equal volume of inert gas (nitrogen, carbon dioxide, steam) at preferably 680°–710° C. over graphite or lustrous carbon at such high speed that the butylene is not in contact with the carbon for more than one second. The carbon is desirably free from iron and alkali, and may be supported on a carrier (silica gel, aluminium or magnesium oxide). In the second application, it is claimed that butadiene is obtained when the dilution with inert gas is very low or zero, but the speed through the carbon has to be increased still further when the butylene is undiluted.

Butadiene has also been obtained by heating such things as naphthenes, terpenes, cyclohexene, cyclohexane, etc., usually at temperatures of 550° C. to 700° C. in the presence of catalysts such as aluminium silicate, calcium aluminate, oxides, phosphates, and chromates on silica gel, platinum, quartz, and strontium uranate.

The most recently disclosed German process developed by Reppe was to condense acetylene with formaldehyde, using copper acetylide catalyst. Butine 1 : 4 diol is formed. This is reduced to tetramethylene glycol, which is then dehydrated to give butadiene.

Chloroprene. The statement about American reluctance to proceed from acetylene must be qualified to cover only straight butadienes, as a basis for synthetic rubber. For the first commercial elastomer—neoprene—was developed by Du Pont de Nemours, and was derived from acetylene.

Actually, of course, acetylene was the raw material employed in the production of chloroprene, the monomer used for making neoprene. Chloroprene is a substituted butadiene. This production was almost entirely due to the fundamental work of Nieuwland [31] on the polymerization of acetylene.

According to Bridgewater,[3] "In 1925 Du Ponts were engaged in research towards the production from acetylene of a synthetic rubber that would excel natural rubber in certain respects, but our results had been most disappointing."

At that time they became aware that Nieuwland had obtained good results for the polymerization of acetylene by using copper catalysts. He was able to provide the essential first step towards the direct manufacture of a butadiene derivative from acetylene that could be polymerized. By means of his methods two acetylene molecules could be made to form a four-carbon chain. By passing acetylene through a highly concentrated solution of cuprous chloride and ammonium

chloride catalysts, he was able to produce monovinylacetylene and divinylacetylene. The method was subsequently outlined by Nieuwland, Calcott, Downing, and Carter.[32] In due course Downing, Carter and Hutton [8] were able to make this a continuous process. Monovinylacetylene is a colourless liquid, b.p. 5° C. having a density of 0·7095.

In one patent Du Pont de Nemours [10] obtained vinylacetylene from acetylene by polymerization in presence of a liquid mass of catalyst comprising water saturated with ammonium chloride and cuprous chloride in proportion 1·7 to 2·2 mols. to 1 mol. cuprous chloride, and not containing more than 0·6 per cent. of HCl, the catalyst being in contact with solid phase components including metallic copper. A temperature of 75° C. is appropriate.

In themselves these derivatives could not supply a satisfactory synthetic rubber; actually they are the basis of satisfactory synthetic resins, finding use for coatings. But the Du Pont team of research workers had the starting point and soon overcame existing difficulties. Carothers, Williams, Collins, and Kirby [5] discovered that monovinyacetylene could be quickly and smoothly converted into 2-chloro-1,3-butadiene. They called this chloroprene. The monovinylacetylene merely required to be treated with hydrochloric acid in the presence of cuprous chloride as catalyst. This was the basis of the first commercial synthetic rubber.

$$3\underset{\text{Coke}}{C} + \underset{\text{Lime}}{CaO} \longrightarrow \underset{\text{Carbide}}{CaC_2} + CO$$

$$CaC_2 + H_2O \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + CaO$$

$$CH\equiv CH + CH\equiv CH \longrightarrow \underset{\text{Monovinyl acetylene}}{CH\equiv C-CH=CH_2}$$

$$CH\equiv C-CH=CH_2 + HCl \longrightarrow \underset{\text{Chloroprene or 2-chloro-1.3-Butadiene}}{CH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2}$$

FIG. 20.—Production of Chloroprene.

Chloroprene is a pungent colourless liquid, boiling at 59·4° C., with a density at 20° C. of 0·9583, and refractive index 1·4583. It is notable for the speed with which it polymerizes spontaneously to form a rubbery polymer.

Production of Vinyl Chloride from Acetylene. The production of vinyl chloride is of major industrial importance. This can best be appreciated from the fact that in the United States in 1947 production

of vinyl plastics was 180 million lbs. Nearly all of this is polyvinyl chloride. The process of manufacture of vinyl chloride from acetylene actually consists of effecting the union of hydrogen chloride with acetylene in the presence of a catalyst.

The patent literature relating to synthesizing vinyl chloride from acetylene may be summed up in a fundamental formula of passing acetylene and hydrogen chloride, compressed up to 1–1·5 atmospheres, over a contact catalyst. The main points of difference among the many variations of this process being the definition of the temperature range, the selection of catalyst and the plant required for the procedure.

The synthesis of vinyl chloride by this method is carried through according to reaction:

$$CH \equiv CH + HCl \longrightarrow \underset{\text{Vinyl chloride}}{CH_2 = C\begin{smallmatrix} Cl \\ H \end{smallmatrix}} + 477 \text{ cals.}$$

The temperature level, with liquid catalysts, in the majority of cases is maintained between 60° and 80° C. The hydrochloric acid solutions of metal chlorides are the most popular catalysts used in the process.

The following reagents are recommended for application as dry catalysts: (*a*) mercuric chloride precipitated on silica gel; in this case the process of obtaining vinyl chloride may be performed at reduced temperatures from 20° to 30° C.; (*b*) activated carbon; here the reaction is conducted at higher temperatures up to 200° C.

The yield of vinyl chloride on the basis of acetylene is usually of the order of 55–70 per cent., and an additional heat economy in the process can be effected by re-circulating exhaust gases.

Judging by the numerous American patent specifications for deriving vinyl chloride from acetylene, it is evident that this method is definitely favoured in the U.S.A.

It is also worth while noting that the rapidly expanding use of the acetylene process for vinyl chloride synthesis in America is paralleled by a similar tendency in Germany. In that country the great reactivity of vinyl chloride, yielding derivatives of far-reaching technical and strategic importance, has been assiduously exploited and manufacture is carried out on a large scale.

Vinyl chloride is a commodity quite amenable to transportation, and may be conveniently carried in steel bottles or in tank-cars.

German Production of Vinyl Chloride. Comprehensive details are now available of the production of vinyl chloride from acetylene at Schkopau. The capacity of the plant was 42,000 tons per annum.

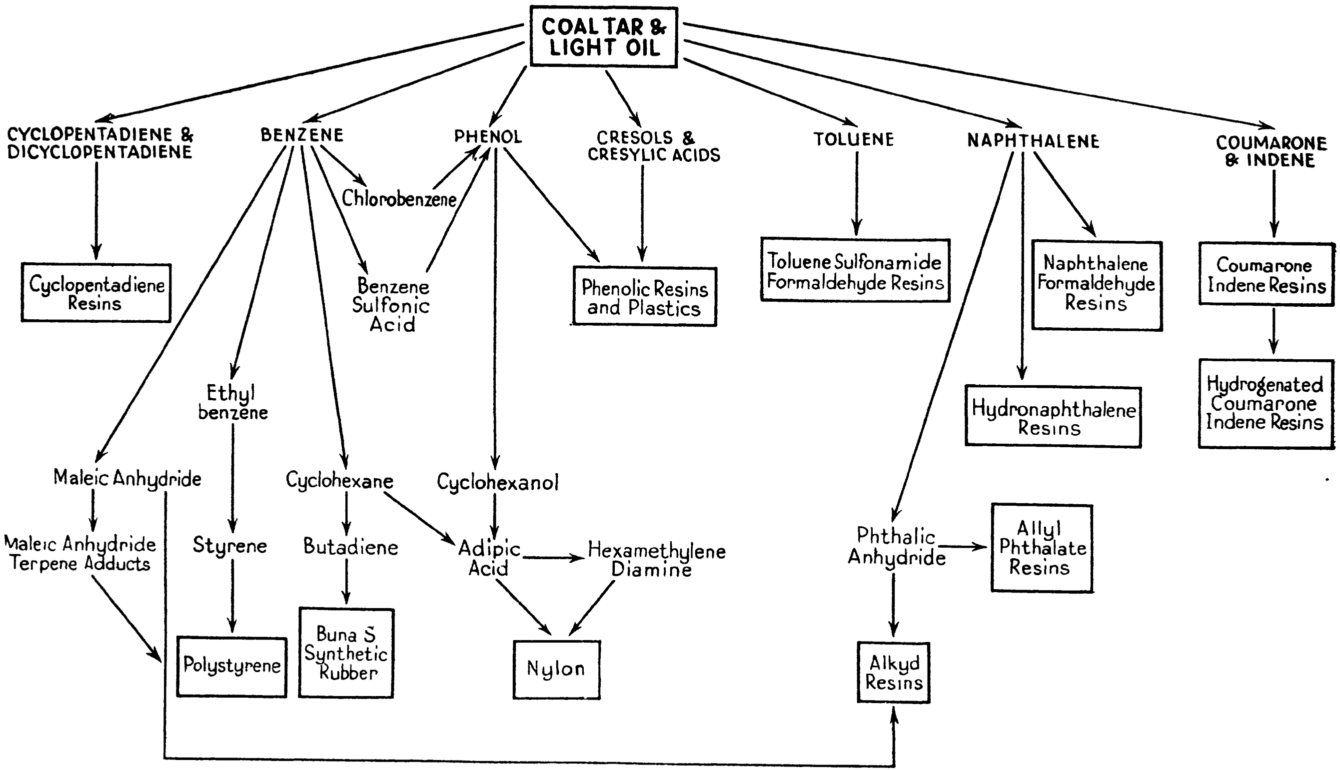

COAL TAR & LIGHT OIL
CYCLOPENTADIENE & DICYCLOPENTADIENE
BENZENE
PHENOL
CRESOLS & CRESYLIC ACIDS
TOLUENE
NAPHTHALENE
COUMARONE & INDENE
Chlorobenzene
Cyclopentadiene Resins
Benzene Sulfonic Acid
Phenolic Resins and Plastics
Toluene Sulfonamide Formaldehyde Resins
Naphthalene Formaldehyde Resins
Coumarone Indene Resins
Hydrogenated Coumarone Indene Resins
Hydronaphthalene Resins
Ethyl benzene
Maleic Anhydride
Cyclohexane
Cyclohexanol
Maleic Anhydride Terpene Adducts
Styrene
Butadiene
Adipic Acid
Hexamethylene Diamine
Phthalic Anhydride
Allyl Phthalate Resins
Polystyrene
Buna S Synthetic Rubber
Nylon
Alkyd Resins

FIG. 21.

The materials used at the Schkopau plant were:

Acetylene:	98·0 per cent. acetylene made from CaC_2 at Schkopau. The acetylene must be dry.
HCl:	95–98 per cent. HCl made by burning hydrogen and chlorine at Schkopau. It must be dry.
Catalyst:	Mercuric chloride on activated carbon. 8- to 14-mesh carbon is soaked in a solution of mercuric chloride and dried. Analysis on dry basis, 90 per cent. carbon and 10 per cent. mercuric chloride.
Calcium chloride:	A 25–30 per cent. solution of calcium chloride for refrigeration purposes.

Vinyl chloride and polyvinyl chloride were produced along the following lines at the I.G. works at Schkopau:

$$\underset{\text{acetylene}}{CH{\equiv}CH} + HCl \xrightarrow{\text{catalyst}} \underset{\text{vinyl chloride}}{CH_2{=}CHCl}$$

Description of Process. The incoming acetylene is thoroughly dried with KOH and the hydrochloric acid with concentrated H_2SO_4. It was emphasized that the reactants must be free of moisture and that catalyst life was dependent on this feature. The reactor is constructed entirely of iron. The catalyst reaction vessel is approximately 10 feet high and 6 feet in diameter. It is mounted vertically and is filled with catalyst tubes each 10 feet long by 2½ inches inside diameter. Each furnace contains an estimated 100 to 150 tubes. Eighteen such units are required for the given production of 3,500 to 4,000 tons per month. The temperature is accurately controlled by circulating cooling water around the catalyst's tubes. The operating temperature with fresh catalyst is 120° C. This is gradually increased to as high as 200° C. over a period of six months to one year. The catalyst is then discarded. It cannot be reactivated, but the mercury is recovered. When a new furnace is put into operation all air is replaced with nitrogen, the furnace is brought up to temperature and the acetylene and hydrochloric acid introduced. The reaction is highly exothermic and good cooling is necessary. It is common practice in Germany to use water for heating or cooling even at temperatures as high as 250° to 300° C. It is extremely simple to remove the heat from the water by flashing off steam.

HCl is always carried in 10 per cent. excess over the acetylene. The reaction is at atmospheric pressure. Pressure drop through the catalyst is less than one pound. The acetylene in the reaction mixture is approximately 10 per cent. Excess HCl is removed with water and the vinyl chloride cooled and condensed by a spray of 25 per cent. $CaCl_2$ solution at − 40° C. Distillation is carried out in two ring pack

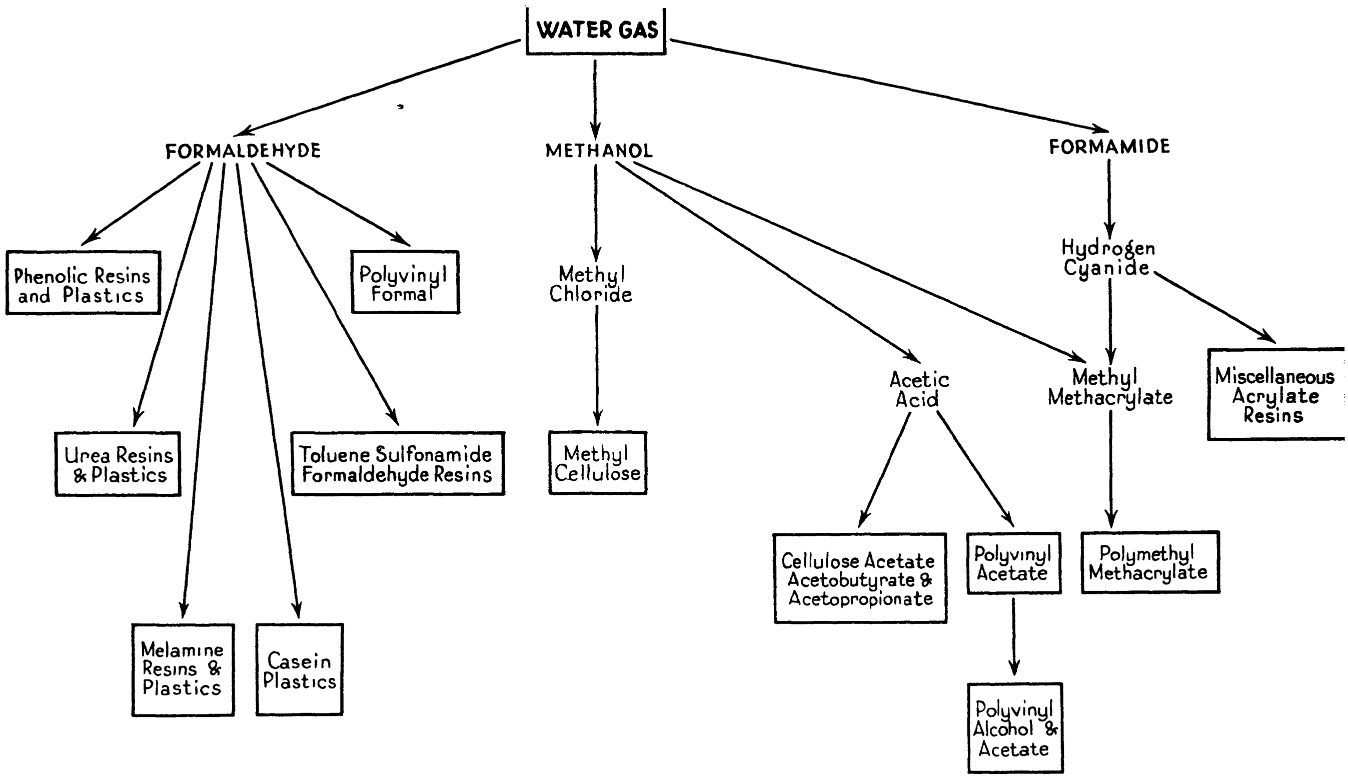

WATER GAS
FORMALDEHYDE
METHANOL
FORMAMIDE
Phenolic Resins and Plastics
Urea Resins & Plastics
Melamine Resins & Plastics
Casein Plastics
Toluene Sulfonamide Formaldehyde Resins
Polyvinyl Formal
Methyl Chloride
Methyl Cellulose
Acetic Acid
Cellulose Acetate Acetobutyrate & Acetopropionate
Polyvinyl Acetate
Polyvinyl Alcohol & Acetate
Hydrogen Cyanide
Methyl Methacrylate
Polymethyl Methacrylate
Miscellaneous Acrylate Resins

FIG. 22.

columns 20 feet high by 36 inches diameter. The first still takes vinyl chloride plus acetylene over the top and residual high-boiling chlorinated compounds out the bottom. (Mostly unsymmetrical ethylene dichloride.) The second takes acetylene overhead and very pure vinyl chloride off the bottom. Yield on acetylene 96–98 per cent., on HCl 80–90 per cent. The vinyl chloride is stored in iron tanks underground at $-40°$ to $-50°$ C. No inhibitor is added. The vinyl chloride is shipped in 60,000-lb. iron tank cars without inhibitor. They are not insulated but do have a wooden housing over them to protect them from the sun. Nitrogen is always used as an inert gas over the vinyl chloride.

Some Further Aspects of the Importance of Coal. It is abundantly clear that coal—through carbide—plays a great part in the production of synthetic elastic materials. This is, however, only part of the story. For the interlocking of plastics with synthetic elastics greatly emphasizes the importance of coal as a source of raw materials. In the preparation of synthetic materials generally, including synthetic elastics, considerable quantities of chemical intermediates are involved. Coal has been the chief source of these intermediates, although in many cases they are now also derived from petroleum products, and on an increasing scale. These include such things as acetic anhydride, acetone, butyraldehyde, ethyl alcohol, ethyl chloride, formaldehyde, hydrogen chloride, methyl methacrylate, methyl alcohol, styrene, vinyl chloride and vinylidene chloride.

Thus synthetic elastics of one sort or another may be derived from the light oil and coal tar obtained by treatment of coal. These will include polystyrene, and the butadiene rubbers. For one method of making butadiene is by cracking cyclohexanes obtained from benzene.

Water gas is of course produced on an enormous scale from coke. This is of the greatest possible importance in connection with such synthetic elastics, which are also, of course, base materials for plastics, as acrylic esters, methacrylic esters, polyvinyl alcohol, etc.

REFERENCES

[1] ACHEMAN, LEHRER and STADLER, Can. P. 393,275/1941.
[2] AMBROS, *Kunststoffe*, 1939, **29**, 106.
[3] BRIDGEWATER, *Ind. Eng. Chem.*, 1935, **27**, 849.
[4] Carbide and Carbon Process, *U.S. Senate Sub-Committee Agriculture and Forestry*, Washington, 1943, p. 1258.
[5] CAROTHERS, WILLIAMS, COLLINS and KIRBY, *J. Amer. Chem. Soc.*, 1931, **53**, 4203.
[6] CHRISTENSEN, *India Rubber World*, 1942, **104**, 477.

[7] Critical Material, *U.S. Senate Sub-Committee on Agriculture and Forestry*, Washington, 1943.
[8] Consortium für Electrochemische Industrie Ges., B.P. 524,849/1939.
[9] DOWNING, CARTER and HUTTON, U.S.P. 1,950,434/1934.
[10] Du Pont de Nemours, B.P. 516,688/1939.
[11] DUNSTAN, *Chemistry and the Petroleum Industry*, 1942, London, p. 20.
[12] EGLOFF, *Ind. Eng. Chem.*, 1938, **30**, 1091.
[13] ELDER, *Ind. Eng. Chem.*, 1942, **34**, 1260.
[14] Fermentation Process, *Rubber Age* (N.Y.), 1942, **52**,
[15] FERNBACH, B.P. 15,204/1911.
[16] FRÖLICH and MORRELL, *I.E.C. News*, 1943, **21**, 1140.
[17] FRYLING, *Ind. Eng. Chem.*, 1947, **39**, 882.
[18] HECHT and REPPE, U.S.P. 2,241,792/1940.
[19] Hercules Powder Co., *Rubber Age* (N.Y.), 1942, **52**, 144.
[20] HURUKAWA, *J. Electrochem. Assn.*, Japan, 1939, **7**, 346.
[21] I.G., B.P. 535,329/1941.
[22] JACOBS, *Ind. Eng. Chem.*, 1939, **31**, 165.
[23] JEFFERS, *2nd Progress Report*, Washington, Feb. 1943.
[24] LEBEDEV, F.P. 665,917/1928.
[25] —— *J. Gen. Chem.*, U.S.S.R., 1933, **6**, 698.
[26] —— Russ. P. 24, 393 1931.
[27] —— B.P. 331, 482/1930.
[28] —— *Zhisn. i Trudui*, Moscow, 1938, 602.
[29] LEUHDEMAN, REPPE and ROTHAAS, Can. P. 392,256/1940.
[30] MCCARTHY, *India Rubber World*, 1942, **106**, 266.
[31] NIEUWLAND, *Science*, 1922, **56**, 486.
[32] NIEUWLAND, CALCOTT, DOWNING and CARTER, *J. Amer. Chem. Soc.*, 1931, **53**, 4197.
[33] Norepol, *Rubber Age*, 1943, **24**, 65.
[34] OSTROMISLENSKY, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1472.
[35] —— *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1495.
[36] PERKIN, WEIZMANN, MATTHEWS and STRANGE, B.P. 5932/1910; B.P. 13,051/1912.
[37] PETRENKO, *Kauchuk i Rezina*, 1940, **4**, 1.
[38] Publicker Process, *U.S. Senate Sub-Committee on Agriculture and Forestry*, Washington, 1943
[39] Reichhold Chemicals Inc., *India Rubber World*, 1942, **107**, 283.
[40] Standard Oil Co. of New Jersey, *India Rubber World*, 1941, **104**, 56.
[41] WAKEMAN and WEIL, *Ind. Eng. Chem.*, 1942, **34**, 1387.
[42] WEIZMANN, B.P. 4845/1915.
[43] WHITMAN, *U.S. Senate Sub-Committee on Agriculture and Forestry*, Washington, 1339.
[44] Combined Intelligence Objectives Sub-Committee, Item 22, File XXII–1.
[45] *Ibid.*, File XXVIII–13.
[46] *Ibid.*, File, XXIX–62.

CHAPTER 7

RAW MATERIALS—PETROLEUM

Oil as a Source of Synthetics. The immediate future of synthetic rubbers is closely connected with petroleum. This is due to the fact that the necessary raw materials may be obtained from this source at a remarkably low cost. The United States, as the world's greatest oil producer, is obviously favourably placed in this respect. As the greatest rubber consumer the question has added importance. It is interesting to note that the next largest oil producer is the U.S.S.R., which is also very actively interested in synthetic rubber production.

It is unnecessary to stress the general importance of oil. As in the case of coal, its primary function is as a source of power. But, while for many years an ever-growing number of commercial materials have been obtained from coal via coal tar, only in recent years has a similar trend set in for petroleum derivatives. The potentialities as a source for synthetic rubber and synthetic resins, etc., add further to its importance.

As petroleum is a major source of olefines, notably ethylene, it is not surprising that the industry should become interested in the growing field of synthetic resins. But as Frölich [15] has pointed out, " Because of its general set-up, the petroleum industry is, as a rule, dependent upon a relatively large scale of operation to obtain the full advantage of its low potential manufacturing costs." So that unless some great industry is affected, progress cannot be very rapid. Obviously, rubber is a major field offering scope for such large-scale operations. Thus the activity with synthetic rubber is likely to bring in its trail the other profound developments with synthetic resins. Without it their progress would be greatly retarded.

Frölich has drawn up the following list of products connected with the general aspect of synthetic rubber which are either now being manufactured wholly or in part from petroleum products, or for which the petroleum industry would be able to supply raw materials.

1. Natural petroleum resins by light hydrocarbon precipitation.
2. Cracking-coil tar resins by condensation of highly condensed petroleum hydrocarbons, such as those which are present in the tar bottoms from the cracking operation, with formaldehyde or ethylene chloride.

3. " Santoresin " by reaction of olefines and diolefines in the presence of aluminium chloride.
4. Polystyrene by polymerization of styrene, which may be produced from ethylbenzene made by alkylation of benzene with ethylene.
5. Polybutylene by polymerization of unsaturated gaseous hydrocarbons to give substantially linear polymers ranging in consistency from

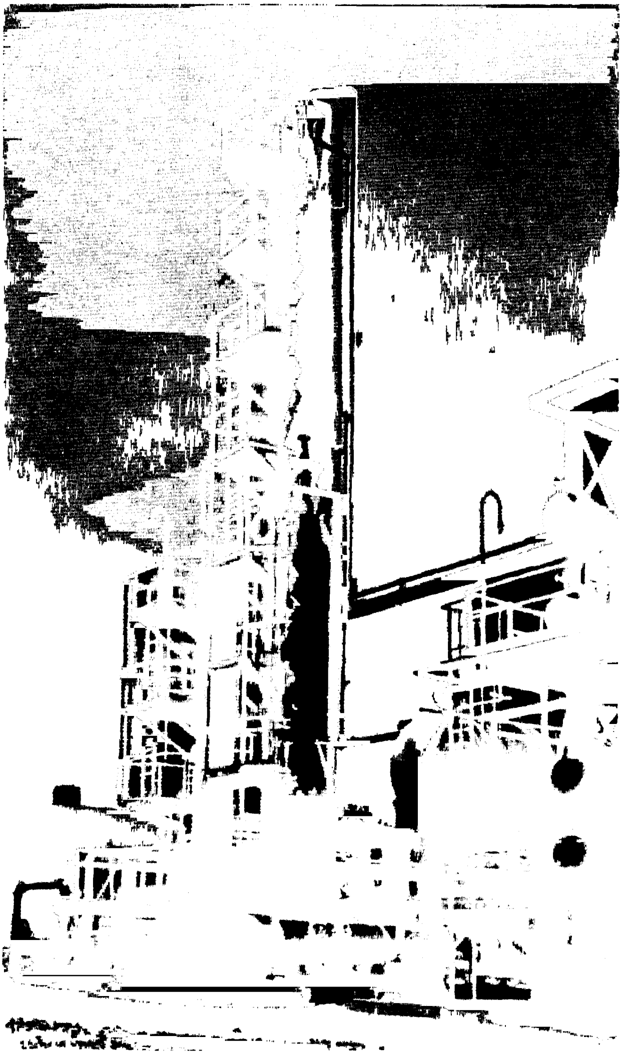


FIG. 23.—Fractionating Tower with Re-boiler

that of a viscous oil to rubbery materials with molecular weights as high as 300,000.

6. " Buna " rubber and similar products by polymerization of butadiene made from acetylene or from *n*-butylenes.
7. Neoprene rubber by polymerization of chloroprene derived from acetylene.
8. " Thiokol " by condensation of sodium polysulphide with ethylene dichloride or other chlorine-containing derivatives.
9. Polysulphones by reaction of olefines with sulphur dioxide.
10. Vinyl resins by polymerization of vinyl chloride and vinyl acetate derived from acetylene or ethylene.
11. Phenol-formaldehyde resins by condensation of formaldehyde with phenols.
12. Alkyd resins by reaction of dibasic acids with polyhydric alcohols—e.g. ethylene glycol and diethylene glycol, from ethylene; and glycerol which may be prepared from propylene.
13. Ethylcellulose by reaction of cellulose with ethyl chloride or diethyl sulphate produced from ethylene.
14. Cellulose acetate by reaction of cellulose with acetic anhydride, which may be derived from ketene obtained by thermal decomposition of acetone produced by dehydrogenation of isopropyl alcohol.
15. Acrylate and methacrylate resins derived in various ways from olefinic compounds.

But particularly in regard to all these activities it has been shown time and time again that so many factors are changed when small-scale results are transferred to commercial unit operations that it is not safe to base commercial operations on small-scale results. This is another reason why full-scale operations with synthetic rubbers have profoundly influenced plastics. Some indication of the scale of operations involved may be derived from the fact that world production of crude petroleum which was 56 million tons in 1914 had by 1945 reached 376 million tons and was still increasing.

Waste in the Oil Industry. The history of oil is probably the most outstanding example of waste. And nowadays whenever there are wastes there is an almost automatic implication of plastics and synthetic rubber. From the time of its discovery in the United States in 1859, oil was prized most highly because of its kerosene content, becoming the fuel for oil lamps. All the low boiling fractions were regarded as a dangerous nuisance and were dumped. The high boiling fractions were equally useless. The arrival of the internal combustion engine in due course completely changed this situation, so that kerosene became very much a secondary material. The once embarrassing fluid now acquired paramount importance as motor fuel. To bring the matter into its right perspective it is estimated that manufacturing cost of petrol in the United States is about 3 to 4 cents

per gallon, while to produce it from coal costs about four times this amount.[2]

As the number of motor-driven vehicles expanded at a terrific rate, petrol production could not keep pace (incidentally, nor could rubber production). The direct distillation method of production was terribly wasteful and inefficient. A shortage appeared imminent. The first step forward came in 1912, when the Burton[6] process of cracking was introduced. Not only was this epoch-making as regards motor spirit production, but it also marked the beginning of synthetic processes based on oil. Since that time there have been numerous effective methods developed for treating oils, including cracking processes, hydrogenation processes, catalytic methods, etc. With each improvement the amount of waste has been decreased, and all sorts of by-products have appeared. More than 2,000,000 tons of chemicals are produced annually from petroleum by-products. About 80 per cent. of this is produced in the United States.

Composition of Petroleum. Petroleum consists of a mixture of hydrocarbons whose composition varies with place of origin. It may contain members of the paraffins, together with cyclo-paraffins and also aromatic hydrocarbons. Nearly always associated with petroleum are gaseous paraffins known generically as " natural gas ".

Straightforward rectification of petroleum yields :

Petrol or gasolene or motor spirit, up to 60° C., consisting chiefly of pentane and hexane.
Benzine distilling up to 90° C., made up largely of hexane and heptane.
Ligroïn distilling up to 120° C.
Kerosene boiling between 150° C. to 300° C.
Heavy oil distilling above 300° C. used for lubricating oils and petroleum jelly.
Tars, asphalts, etc.

Natural Gas. A great deal has been heard about " natural gas ". Natural gas consists of a mixture of gaseous paraffins, chiefly methane, ethane, propane, butane and isopentane. Wherever petroleum is found there is generally a certain amount of natural gas about. However, the gas does occur frequently alone without any associated petroleum. According to Dunstan,[12] the composition of a typical example is as shown in Table 44. There are many seemingly unlimited subterranean reservoirs which when tapped blow off in a spectacular manner. Enormous amounts are available in the United States and in the U.S.S.R. In the United States about 45 per cent. comes

from oil wells. For many years all natural gas was allowed to blow off to waste into the air.

This natural gas is expected to be the primary source of raw materials for synthetic rubbers and synthetic resins. In recent years a certain amount has been stripped for petrol. In the United States,

TABLE 44. THE MAIN CONSTITUENTS OF NATURAL GAS

	M.p. ° C.	B.p. ° C.
Methane	−182	−161
Ethane	−172	− 89
Propane	−187	− 42
n-Butane	−135	− 0·6
iso-Butane	−145	− 10
n-Pentane	—	+ 37

for a number of years, a large proportion of natural gas has been used to perform the functions carried out by coal gas, which it does more efficiently. There is a network of natural-gas pipe-lines spreading all over the American Continent. In other countries this activity is more localized.

Another great industry based on natural gas is the manufacture of channel black, made by burning the gas under special conditions. Thus the production of carbon black in the United States, according to the Bureau of Mines, in 1941 was 504 million lbs. In 1946, due almost entirely to the added demand for synthetic rubbers, the total was 1,227 million lbs. In this connection we come across a very ironical situation. The rubber industry has expanded to its present volume mainly on the merits of one product—the tyre. Tyres owe their remarkable wearing and service properties almost entirely to the presence of large amounts of carbon black, which reinforce the rubber to a remarkable degree. No satisfactory explanation of this phenomenon has yet been put forward. The vast bulk of carbon black produced goes into tyres. It can fairly be claimed that rubber owes much of its importance to carbon black, and through this, to the " natural gas " from which carbon black is made. Now there is every prospect of the same " natural gas " producing potentially serious competitors for rubber. It should be made clear that carbon black is of equally fundamental importance to the performance of every synthetic rubber.

In spite of these applications of natural gas, the major portion of available gas is still being wasted into the atmosphere. As raw material for any products it is there for the asking It is not to be wondered that the petroleum concerns are interested in the possibilities which may lead to major uses. According to Grosse and Ipatieff,[16] there is

available in the United States annually from all sources 300 billion cubic feet of ethane, 120 billion of propane, and 70 billion cubic feet of butanes.

Some of the Leading Processes. The processes which lead to those products, which may form the basis for synthetic rubbers and synthetic resins, are briefly as follows :

Cracking Processes with Oils. Cracking is a heat treatment which converts hydrocarbons of relatively high boiling points and high molecular weights into materials of lower boiling points and low molecular weights, suitable for use as motor spirit. Cracking divides large molecules into smaller units. It results in an increase in the amount of total motor spirit obtained from crude oils. These oils may be cracked under high pressure in the liquid form, or at higher temperatures as gases. Invariably large quantities of gaseous products are obtained, consisting mainly of olefines and some diolefines.

In effect cracking is the thermal decomposition of heavier hydrocarbon molecules into simpler molecules. According to Dunstan [12] 100 gallons of cracking stock will yield something like 60 gallons of petrol. The residue will be heavier oil together with gas and coke.

Cracking Processes with Gaseous Hydrocarbons (i.e. natural gas). Gaseous hydrocarbons are submitted to high temperatures when dehydrogenation occurs with the formation of olefines. The paraffins tend to produce simpler molecules of the corresponding olefine, sometimes lower paraffins and often hydrogen. Thus, with the exception of methane, the paraffins such as ethane, propane, *n*-butane, and isobutane, yield olefines such as ethylene, propylene, and three isomeric butylenes.

The decomposition takes hours at 400° C., but only seconds at 800° C. It is very profoundly influenced by catalysts, such as chromium oxide, molybdenum oxide, vanadium oxide, together with aluminia or magnesia, activated charcoal, zinc-chromium alloy, etc., all of which facilitate dehydrogenation at lower temperatures, about 350° C.

The following account by Grosse, Morrell and Mavity [17] clearly explains the position :

The dehydrogenation of the paraffin gases to the corresponding olefines is the problem of fundamental importance to the oil industry. The technical problem of efficiency converting gaseous olefines into liquid motor fuel has

been solved within recent years by both catalytic and purely thermal processes. Therefore a process for the conversion of paraffins into olefines would put to good use all the paraffin gases except methane. These gases are available in enormous quantities from such sources as natural gas, and gasolene, petroleum, petroleum gas, gas from the cracking processes, coke-oven gas, and refinery gasolene.

TABLE 45. FORMATION OF CONJUGATED DIOLEFINES BY DEHYDROGENATION

Compounds Dehydrogenated	Temp	Contact Time	Diolefin Name	Diolefin Yield	Un-reacted Charge	Carbon
	° C.	Sec.		Wt. % of charge	Wt. %	Wt. % of charge
n-Butenes . . .	600	0·75	1,3-Butadiene	18	50	11·2
n-Butenes . . .	600	0·34	1,3-Butadiene	20·6	59	4·8
3-Methyl-1-butene .	600	0·5	Isoprene	21·4	34	12·8
2-Methyl-1-butene + 2-methyl-2-butene	600	0·39	Isoprene	22·3	44	6·2
2-Pentene . . .	600	0·40	Piperylene	30·3	44	7·6
Cyclopentane . .	500	1·85	Cyclopentadiene	8·9	62	8·8

A catalytic dehydrogenation process has been developed for converting normal and isobutane, propane, butane and ethane to the corresponding olefines. The process briefly consists in passing the pre-heated gases over a suitable catalyst. The outgoing gases contain olefine and hydrogen besides the unreacted original paraffins. The olefines are polymerized or used in alkylation. The hydrogen is separated and the unreacted original paraffins are recycled.

The plant consists essentially of a furnace, banks of catalyst reactors, and hydrogen separation units. Automatic controls alternate the flow of paraffin gases first through the furnace and one section of reactors, and then through another, while the catalyst is being regenerated in the first section. The regeneration consists in passing automatic control amounts to air mixed with composition gases or steam to burn off the carbon on the catalyst at a moderate composition temperature, usually below 900° C. A feature of the process is that the length of operating cycle is short, usually of the order of one hour. The advantages of the catalytic process over purely thermal cracking are the much larger over-all yields of the corresponding olefines and a much higher reaction velocity.

According to Frey and Hepp[14] the reactions which occur and the yields which are obtained under different conditions are illustrated in Table 46.

TABLE 46. CONVERSION OF PARAFFINS TO OLEFINES

Reaction			*Yield of Olefine*
$CH_3.CH_3$ ethane	$\longrightarrow CH_2{=}CH_2$ ethylene	$+H_2$	100%
$CH_3.CH_3.CH_2$ propane	$\longrightarrow CH_3.CH{-}CH_2$ propylene	$+H_2$	45%
	$\longrightarrow CH_2{=}CH_2$	$+CH_4$ methane	55%
$CH_3.CH_2.CH_2.CH_3$ *n*-butane	$\longrightarrow CH_3.CH_2.CH{=}CH_2$ 1-butene	$+H_2$	12%
	$\longrightarrow CH_3CH{-}CH.CH_3$ 2-butene	$+H_2$	12%
	$\longrightarrow CH_3.CH\ \ CH_2$	$+CH_4$	50%
	$\longrightarrow CH_2\ \ CH_2$	$+CH_3.CH_3$	
	high temperature $\longrightarrow 2CH_2{-}CH_2$	$+H_2$	38%
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_3$ iso-butane	$\longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\ \ CH_2$ iso-butylene	$+H_2$	60%
	$\longrightarrow CH_3.CH\ \ CH_2$	$+CH_4$	40%
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$ neo-pentane	$\longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\ \ CH_2$	$+CH_4$	100%

In fact, the paraffins, with the exception of methane, can be catalytically dehydrogenated to the corresponding olefines according to the general reaction :

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2$$

In this manner, and in almost every treatment of petroleum fractions, vast quantities of a whole range of olefines can be obtained. There are other processes such as alkylation, isomerization, etc., but these have not such a pronounced bearing on synthetic rubbers and plastics.

To maintain the sense of proportion it should be added that hitherto the main urge has all the time been to produce more motor spirit. Indeed, during the last twenty years, the amount of petrol obtained from a given amount of crude oil has doubled. The olefines lend themselves very readily to conversion into such products, since they polymerize quite easily under heat and pressure to yield liquid hydrocarbons in the petrol range.

On the other hand, chemical manufacturers have concentrated on developing cracking conditions which give maximum production of simple olefines and a minimum production of motor spirit. While this applies to ethylene and propylene without qualification, the butylenes are not quite so amenable, and other uses have been sought for them. The influence of various catalysed treatments of isobutylene,

for example, has led to the production of the polyisobutylene range of materials—ranging from very viscous liquids up to extremely rubbery products.

One of the chief conditions required for a reasonably economic production of synthetic rubbers is evidently satisfied. A cheap unlimited source of compounds having four carbon atoms in a row is available. Since these compounds are already unsaturated the conditions are even more favourable.

Petroleum Processes. According to Frölich and Murphree:

Butadiene is one of the many products formed by thermal cracking of petroleum hydrocarbons. In the so-called liquid phase cracking to produce petrol, which is carried out at temperatures of the order of 450° C. and pressures upward of 1,000 lb. per square inch, the amount of diolefinic material formed is very small. If the cracking temperature is raised, however, there is an increased tendency toward the formation of butadiene and other diolefines. In the case of true vapour phase cracking carried out at high temperature and low pressure, their concentrations reach appreciable values. Because of the thermodynamic instability of butadiene and its marked tendency to undergo polymerization and condensation reactions, the yields obtainable are greatly benefited by maintaining low partial pressure in the cracking zone and by employing rapid chilling of the cracked material to temperatures which diminish its chemical activity.

Elder [13] lists the following methods of operation which have been employed to attain this result:

1. Charging stock is mixed with superheated steam.
2. Steam-hydrocarbon mixtures are direct-cracked in regenerative furnaces.
3. A definite amount of air is added to burn some of the charging stock, thereby raising the temperature of the stock.
4. Hot flue gas at temperatures as high as 3,000° F. is used to raise the temperature of the charging stock by direct mixing.

Until quite recently, however, practically all of the butadiene produced in this country from petroleum sources was derived from such high-temperature cracking.

In addition to butadiene, thermal cracking of gas oils or naphthas at high-temperature levels also yields other useful products, including large quantities of olefines and aromatics. There is, therefore, a close connection between the manufacture of butadiene by this method and the production of high-octane number aviation fuel. Murphree gives the following data from steam cracking of heavy naphthas which illustrate this relationship:

Other conditions being equal, the yield of butadiene increases for different feed stocks in the following order: (*a*) aromatics, (*b*) paraffins, (*c*) olefines,

(*d*) naphthenes (cycloparaffins), (*e*) unsaturated naphthenes (cyclo-olefines). According to published technical data and patents, cyclohexane and cyclohexene give particularly high yields of butadiene by straight thermal cracking at high temperatures and preferably under reduced pressure.

When cracking petroleum fractions, the yield of butadiene under comparable conditions increases as the boiling-point of the cut decreases. By way of illustration, gasoline gives a higher yield than kerosene or gas oil fractions derived from the same crude source.

Butadiene can also be produced from butane or the butenes. If butane is the starting material, it is first converted to butenes and then to butadiene by successive dehydrogenation:

$$C_4H_{10}=C_4H_8+H_2$$
$$C_4H_8=C_4H_6+H_2$$

Where butenes are available from oil-cracking operations, they may be converted directly to butadiene without going through the former step. In order to obtain good yields it is necessary to carry out these operations with a catalyst.

Several petroleum companies have worked on the production of butadiene from butane. Processes contributed by the Universal Oil Products Co., the Phillips Petroleum Co., and the Catalytic Development Co. (Houdry) are incorporated in the synthetic rubber programme. In all these operations dehydrogenation of the butane is first carried out to produce butylenes. They may either start directly from butane, or a mixture of butane and butylenes is supplied to the second step of the operation where the major portion of the butadiene is produced.

Other petroleum companies have worked on catalytic processes for converting butenes, such as would be produced either from butane or from petroleum cracking, into butadiene. The method now being used has been worked out by the Standard Oil Development Co. The basic operation in this case is the dehydrogenation of butenes to butadiene with a suitable catalyst. According to Murphree, the source of butenes is from petroleum cracking and particularly from a new catalytic cracking process which yields large quantities of butenes.

These catalytic operations will account for most of the butadiene produced in the rubber programme. As in the case of the alcohol process, no extensive technical information has been published to date. In general, however, all such petroleum operations require reactivation of the catalyst because of gradual build-up of coke deposit. This means a cycle operation involving reaction and reactivation in regular sequence.

Ethylene again a Leading Product. For the moment let us refer

back to ethylene. Its importance to the plastics industry cannot be over-stressed. Something has already been described about its potentialities for the production of alcohol. This is being energetically pursued. It is estimated that the potential capacity of the oil industry in the United States is more than 1,000 million gallons of alcohols per year from cracked gases alone. This includes ethyl alcohol, propyl alcohols, butyl alcohols, etc., all of great importance to plastics, lacquers, and many other industries. At the present time these olefines are being used for the manufacture of numerous glycols and related compounds. And indeed quite recently it has been stated that a commercial plant for the production of glycerol has begun to operate. The implications of this activity in relation to alkyd resins are obvious.

While most emphasis has been laid upon the use of butadiene elastomers, because most types are derived from it, yet we must remember there are others. Their raw materials have not yet been discussed, because these products are anomalous (or appear to be so at present). For example, Thiokol is based upon ethylene dichloride and various inorganic polysulphides.

Ethylene dichloride, in itself a very valuable and widely used solvent, is made by direct combination of ethylene and chlorine.

$$Cl_2 + CH_2 = CH_2 \longrightarrow CH_2Cl—CH_2Cl.$$

Thus another synthetic rubber-like material has a direct tie-up with the petroleum industry.

Recently ethylene dichloride has acquired a greater significance from the plastics angle as a source for vinyl chloride. By virtue of its rubbery properties polyvinyl chloride comes into consideration as a leading member of the group of elastoplasts. Brous,[5] of the Goodrich Company, has produced vinyl chloride by heating ethylene dichloride in the presence of methyl alcohol and adding aqueous sodium hydroxide.

Ethyl chloride may be synthesized via ethylene or hydrogen chloride. Interacting with benzene under the influence of aluminium chloride it gives ethyl benzene, from which styrene is derived—essential for Buna-S rubbers.

The Production of Synthetic Rubber Raw Materials. Reviewing this position, it is evident that, so far, it has only been shown that the petroleum industry is on level terms with coal, acetylene, etc., which have previously been described, possibly with raw materials somewhat cheaper. If this were so then there would be no overwhelming advantage, as against the other raw material sources. The same lengthy series of synthetic processes would be necessary to produce

the synthetic rubber monomers. Clearly the olefines are available cheaply and in unlimited quantity. This is not enough.

It is axiomatic that the development of the synthetic rubber industry depends upon the production of cheap butadiene and isoprene.

For the oil industry to be well and truly leading in this field, the ultimate raw material—butadiene (or possibly isoprene) was, therefore, necessary.

Butadiene is found in petroleum in small quantities. As far back as 1933 large-scale work was being carried out in the U.S.S.R. to recover butadiene from petroleum. In the aggregate the amount would be very large, but the difficulties of separating it are considerable.

Butadiene is extremely difficult to separate from other constituents. One method is to prepare the yellow solid compound with cuprous chloride or hydrogen chloride. When heated at 30–100° C. pure butadiene in high yield is obtained. Many materials enhance the effect of the cuprous chloride solution, including ammonium chloride, stannous chloride, sodium chloride, and ethylene glycol. A certain amount is available in the butene fraction separated from the gas produced industrially by the vapour phase (high-temperature) cracking of oils. According to Brooks and Ellis,[4] such a fraction contained:

	Per cent.
Butenes	10–12
Isobutene	20–24
n-Butenes	50–55
Butadiene	12–14
C_2 and C_5	2

According to Grosse, Morrel and Mavity,[17] the fundamental requirement was to find " the connecting link between the billions of cubic feet of butanes present in natural and cracked gases, and of butenes present in the latter, and the billions of gallons of pentanes available in natural gasolene and crude oil on the one hand, and the production of synthetic rubber from these raw materials on the other ". This has been found, in the catalytic dehydrogenation of olefines to diolefines (or dienes).

Olefines can be further dehydrogenated with the same catalysts (chromium, molybdenum, or vanadium oxide on aluminia) to diolefines. The diolefines formed are of the conjugated type and have the same carbon framework as the parent olefine. Other catalysts used include tungsten, titanium, zirconium, cerium, and thorium oxides, notably for dehydration of butylene.

Thus from 1- or 2-butylene, 1,3-butadiene is formed; from straight-chain pentenes, piperylene (1,3-pentadiene); and from

branched-chain pentenes, isoprene (2-methyl-1,3-butadiene). The original position of the double bond in the framework of the olefine is probably of no consequence since, especially in the presence of the alumina base catalyst, it is freely shifted. Thus isoprene was obtained in approximately equal yields from either 3-methyl-1-butene or from a mixture of 2-methyl-1-butene and 2-methyl-2-butene.

Cracked Gas
Fractionation

Ethylene and others
Ethanol
Aldehyde
Aldol
Hydrogenation to 1,3-butylene glycol
Dehydration to butadiene

C_4 gases
Butadiene by dehydrogenation of butane

Liquid oils
Fractionation producing
—Other products
Benzene
Ethyl benzene
Styrene

Emulsification and Polymerization
BUNA-S

FIG. 24.- Buna Rubber from Cracked Gas.[12]

According to Brooks [3] diolefines, such as butadiene, isoprene, cyclopentadiene, etc., could be separated from mixtures containing olefines by passing through finely divided cuprous chloride in water. These diolefines are produced by pyrolytic methods which are less drastic than those required for the conversion of olefines into motor fuel.

According to the Dow Chemical Co.,[10] butadiene is separated from mixtures with other hydrocarbons having four carbon atoms, such as the butylenes and butanes by fractionally distilling the liquefied hydrocarbons in the presence of liquid ammonia.

Work along somewhat similar lines in Germany has been described by Schulze and Schulze.[22]

Grosse, Morrell and Mavity (loc. cit.) have described some very successful processes. The charge of gas was passed at a definite rate over granular catalyst at reduced pressure (0·25 atm.) and at

temperatures between 600° and 650° C. The catalysts were oxides of chromium, molybdenum, or vanadium on aluminia.

Single pass yields were of the order of 20–30 per cent. diolefine, while recycled yields were up to 79 per cent.

The crux of the whole matter is that processes, which resemble the ordinary everyday processes being carried out in the refineries in existing plant, produce butadiene, etc., ready for conversion into synthetic rubber.

The Weizmann Process for Producing Aromatics from Petroleum. The Weizmann Process (also known as the Catarole Process) is a most important development in petroleum treatment. It is a process for the catalytic production of aromatics and olefines from crude petroleum fractions. The successful conversion of paraffins and naphthenes into aromatic compounds is of profound significance. Many of the products are involved in synthetic rubber and plastics manufacture. The process was developed by Weizmann, Bergmann and Kind,[30] in Great Britain.

Outline of Process. A petroleum distillate, obtained by the straight distillation of crude oil, with a boiling range somewhere between 225° and 500° to 550° F., is heated, evaporated, and then passed at temperatures between 1100° and 1250° F. through tubes filled with a catalyst in which the hydrocarbon molecules are broken up and rearranged. For this part of the process a large heat input is necessary in order to provide the energy for the foregoing conversion. The reaction product is then passed, still at the same temperatures, through reactors filled with the catalyst where the molecules are finally rearranged and the complete conversion takes place. On leaving this final reactor the reaction product is cooled down and those hydrocarbons which are gaseous at normal temperature are separated from the liquids.

The charging stock is a mixture of various hydrocarbons, mainly paraffins and hydroaromatics, with sometimes a small percentage of branch-chain aromatics. The reaction product consists roughly of substances which are half liquid and half gaseous (at ordinary temperatures and pressures). The liquid part is made up almost exclusively of aromatics, and the gases contain roughly two-thirds of the valuable olefins (ethylene, propylene and butylenes, including butadiene), the remainder being mainly methane and ethane.

The process can work continuously for periods of 50 to 70 hours before the pressure in the system builds up (because of deposits of pitch and carbon on the catalyst) when the plant is switched off and, without substantial change in the temperature of the furnace, a mixture of air and flue gases or steam is passed through the tubes and reactors. After

8 to 10 hours the carbonaceous deposits are burned off and the cycle can start again.

In order to obtain from the liquid reaction product the aromatics—benzene, toluene, xylenes, styrene, alkylbenzenes, indene resins, naphthalene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene and chrysene—in the very pure form required by modern industry, separation by means of sharp distillation and fractionation with subsequent chemical treatment is necessary. The solid aromatics, such as naphthalene and anthracene, are further purified by recrystallization. These processes can be carried out in the conventional way developed over the last hundred years in the coal-tar industry. For some a different technique has been developed which utilizes the great technical advances made in the petroleum industry in recent years.

Separation of Olefinic Gases. To separate and obtain in great purity the olefinic gases (ethylene, propylene, butylenes, and butadiene), which all have boiling-points well below the freezing-point of water, the same team has devised a method by which, through

TABLE 47. CATAROLE PRODUCTS

	Yields varying from	to
	(weight	per cent.)
(A) Gases varying from 45 to 63 per cent. by weight:		
Hydrogen	0·5	0·9
Methane	15·0	20·0
Ethylene	7·0	12·0
Ethane	6·0	10·0
Propylene	9·0	10·0
Propane	1·0	2·0
Butylenes and butane	2·0	6·0
(B) Liquids varying from 36 to 54 per cent. by weight:		
Below benzene	0·5	1·5
Benzene	6·0	11·0
Toluene	5·0	11·0
Xylenes	3·5	7·0
Alkylbenzenes and indene resins	3·5	8·0
Boiling above 360° F.	13·0	24·0
Naphthalene, Anthracene, Phenanthrene, Chrysene, Pyrene	2·0	3·0
(C) Losses	1 to 3 per cent. by weight	

compression and refrigeration (cascade method), all the gases (apart from methane and hydrogen) are first liquefied (for which purpose temperatures as low as – 200° F. to – 250° F. have to be applied) and then fractionated by distillation. This method is simple and efficient, but requires complicated equipment in order to reduce the operating costs. As a means of separating gases it may well find many applications in the future.

In accordance with the chemical composition and boiling range of the charging stock to the Catarole plant, and by varying the conditions of operation, the proportion of the liquid, solid and gaseous end products can be altered within wide limits. This flexibility, as shown by Table 47, is of fundamental importance in a process which yields most of the basic raw materials required for an industry subject to such rapid changes as the chemical industry.

Cramer [9] has summarized the various methods for producing butadiene practised in the United States.

TABLE 48

1. $\text{Petroleum} \xrightarrow[\text{cracking}]{\text{normal}} CH_2 \;\; CH—CH \;\; CH_2$ ($\frac{1}{2}$ to $\frac{3}{4}$%)

2. $\text{Petroleum} \xrightarrow[\text{cracking}]{\text{special}} CH_2—CH \;\; CH—CH_2$ (5 to 12%)

3. $CH_3.CH \;\; CH.CH_3 + Cl_2 \longrightarrow CH_3.CHCl—CHCl.CH_3$

$$\xrightarrow[\text{BaCl}_2]{\text{Heat with}} CH_2 \;\; CH—CH \;\; CH_2 + 2HCl$$

4. $CH_3.CH_2.CH_2.CH_3 \xrightarrow[\text{at 600° C.}]{Al_2O_3 + Cr_2O_3} CH_3—CH{=}CH—CH_3$

$$\xrightarrow[\text{at 650° C.}]{Al_2O_3 + Cr_2O_3} CH_2 \;\; CH—CH \;\; CH_2 + H_2$$

5. $\text{Acetylene} \xrightarrow[NH_4Cl]{Cu_2Cl_2 \text{ and}} CH_2{=}CH—C{\equiv}CH$

$$\xrightarrow[\text{hydrogenation}]{\text{selective}} CH_2—CH—CH—CH_2$$

These processes have been developed to a very high pitch of efficiency.

Concentration and Purification. Butadiene as produced may be accompanied by other C_4 hydrocarbons. The following is a complete list of this family of compounds and their boiling-points :

TABLE 49

	B.p. ° C.
Isobutane	−11·7
Isobutylene	− 6·7
Butene-1	− 6·2
Butadiene-1,3	− 4·5
n-Butane	− 0·5
Trans-butene-2	+ 1·0
Cyclobutene	2·4
Cis-butene-2	3·7
Methylcyclopropane	4·5
Vinyl acetylene	5·0
Ethyl acetylene	8·6
Methyl allene	10·3
Diacetylene	10·3
Cyclobutane	13·1
Dimethyl acetylene	27·1

The extent to which these other hydrocarbons are present depends upon the method by which the butadiene is made. Kolachov [19] states that the glycol process is the only one that will deliver 98·5 per cent. pure butadiene directly from the converter. The aldol method probably produces a similar result. But the remaining 1·5 per cent. may be detrimental to the subsequent polymerization of the butadiene into rubber.

Contamination with Butylenes.—The production of butadiene by the alcohol process leads to some contamination with butylenes. Contaminated butadiene seems to have been used successfully by the Russians in their sodium polymerization process. In the case of the Buna-S emulsion polymerization process the requirements in regard to purity are more rigorous. In general, butadiene from petroleum cracking presents complex mixtures. As the temperature is increased, unsaturation increases. Butadiene, acetylenes, and allenes are therefore present in greater concentrations, the higher the temperature of cracking.

From the boiling-points given above it will be noted that the removal, particularly of butene-1 and isobutylene, cannot be accomplished even by the most efficient methods of distillation. However, Frölich and Murphree described how certain materials have been found which, when added to such a mixture, depress the volatility of the butadiene to such an extent that the olefines can actually be boiled off in advance. This is the azeotropic distillation and forms the basis for several commercial methods of concentrating butadiene to a purity of some 99 per cent.

Another means of separating butadiene from hydrocarbons accompanying it is based on the formation of intermediate chemical com-

pounds. Thus, certain systems containing copper, mercury, and silver salts will combine chemically with olefines, diolefines, and acetylenes, but not with paraffinic constituents. By taking advantage of the relative stabilities of these addition compounds, it is possible to regenerate selectively the butadiene in highly concentrated form. This principle forms the basis for another process by which butadiene is being made in a degree of purity suitable for polymerization into synthetic rubber.

As a result the petroleum industry bears the main brunt of producing butadiene for the American synthetic programme. So much

TABLE 50. VAPOUR PRESSURE OF 1,3-BUTADIENE [7]

	lb./in.^{2}
− 130° F.	0·08145
− 94	0·4364
− 68	1·6290
− 22	4·7900
− 4	7·623
+ 14	11·8300
24	14·7500
50	25·6100
86	51·400
104	70·090
140	124·200
176	203·7

so that during the war a number of adjustments were found necessary in the industry. The Baruch Committee recommended that there should be a reduction of petrol output in favour of butadiene, while cracking plants should be converted to the production of butadiene.

The preparation of enormous quantities of butadiene has introduced a variety of storage problems. Since butadiene is a gas at ordinary temperatures, the problem is not altogether simple. A great deal of work has been carried out on it. Another complication is the fact that butadiene tends to polymerize under the influence of active oxygen, whether as air, or as oxygen, or as inorganic or organic peroxides. Moreover, the rate of high molecular polymerization has been shown to be directly proportional to the square root of the concentration of peroxide or active oxygen.

In this connection it is found that in butadiene plants and monomer recovery units there is a tendency for the formation of benzene-insoluble material resembling " popcorn " and known by that name. It is able to grow rapidly when exposed to monomer. Kharasch [20] has shown that the growth of " popcorn " can be deactivated with nitrogen dioxide or commercially by means of sodium nitrite solution.

It has been established that the best type of storage container is a

vapour-tight air-free vessel. It has been suggested that it should be an insulated and refrigerated double-walled cylindrical container with a suspended bottom and a dome roof. In the United States these have been designed for a working pressure of 3 lb. per square inch and are kept at 32° F.

There is another extensively interesting development which brings petroleum and agricultural activities closer. This is the enormous demand for furfural which is to be used as a selective solvent in the various stages of manufacture of butadiene. The richest sources of furfural are oat hulls, cotton-seed hulls, and corn cobs. About 10 lbs. of these raw materials yield 1 lb. furfural. Here is yet another example of how synthetic rubber production will affect plastics, for this particular activity will have repercussions on the manufacture and use of furfural resins.

Russian Work on Butadiene Derived from Petroleum and its Fractions.[21] Considerable attention has been focused in the United States and abroad on petroleum products as a cheap source of butadiene. Although the process is apparently not in large-scale operation in Russia, on account of the fact that the alcohol process is the more efficient of the two under conditions of Russian economy, extensive research has been done by Russian investigators on this subject.

It is well known that the thermal decomposition of petroleum yields quantities of butadiene, together with isoprene and other diolefines. Work was done to establish the processing conditions most favourable to the formation of 1,3-butadiene from products of the Russian crude-oil industry.

Petroleum product from the Baku region of the Caucasus, known to be rich in naphthenic hydrocarbons such as cyclohexane (b.p. 75° C.), methylcyclohexane (b.p. 100° C.) and 1,3-dimethylcyclohexane (b.p. 120° C.), were used.

In view of the fact that butadiene is unstable at high temperatures, the method involved a short heating and a subsequent rapid cooling (quenching) of the gaseous decomposition products. Neither substantial reduction in pressure nor dilution with inert gases was used, although such procedures are known to increase the yield of butadiene.

Only two conditions were varied, the temperature and the speed of flow of the material through the heated zone of the apparatus (a quartz tube). The products investigated and the results obtained are shown in Table 51.

The investigators came to the conclusion that:

1. The yield of butadiene obtained as a result of thermal decomposition (pyrolysis) of various petroleum fractions varies within wide

TABLE 51

No.	Substance	Density d_{15}	Flash point (° C.)	Viscosity at 20° C.	Optimum butadiene (percentage)	Best temp. (° C.)	Optimum flow (c.c. per min. per sq. cm. cross-section)
1	Gasoline . .	0·7495	—	—	11	750	0·48
2	Kerosene. .	0·8247	—	—	5·22	750	0·46
3	Lubricating oil	0·8862	146	2·54	3·91	735	0·16 0·24
4	Crude oil .	0·8952	42·3	4·68	3·73	750	0·43
5	Mazout . .	0·9351	152	—	2·55	715	0·36

In addition, the following individual fractions of gasoline were investigated :

6	77–85° C.	0·7036	—	—	7·50	750	0·45
7	101–103° C.	0·7364	—	—	11·00	750	0·45
8	117° C.	0·7599	—	—	8·37	750	0·45
9	120·6° C.	0·7707	—	—	7·41	750	0·45

limits. Mazout gives the lowest yield (2·5 per cent.). The yield is higher for lubricating oils and kerosene and reaches its maximum for gasoline (11 per cent.). The various fractions of gasoline again yield varying amounts of butadiene.

2. The optimum temperature of the pyrolysis is higher for the lighter fractions of petroleum than for the heavier ones. For Mazout it is 715° C., for gasoline it is 750° C.

3. The optimum speed of passage varies only to a small extent from product to product, and is found to be in the region of 0·4–0·5 c.c. per min. per sq. cm. of cross-section.

4. For heavy fractions, the yield declines only slightly when deviating from the ideal conditions ; for the light fractions, however, the yield is considerably decreased.

Direct Processes from Petroleum. Petroleum chemists have not been content to leave the matter here. It has been maintained by one leading group that synthetic rubber should be obtainable from refinery gases by even more direct methods than have existed. These members of the Esso laboratory of the Standard Oil Development Co. are familiar with every aspect of synthetic rubber production. They understand all the implications of butadiene rubbers, for eleven years ago Standard Oil entered into a working arrangement with I.G. Farbenindustrie to exchange and share research developments.[23] Arising from this it becomes clear why polyisobutylene, for example, has only been available from these two sources—as Oppanol made by the I.G., and as Vistanex made by Standard Oil. Just before the

war, Standard Oil traded some of its oil technology patents for exclusive United States' rights to manufacture Buna.

The first notable success of petroleum chemists in the synthetic rubber field was with polyisobutylene. There are a number of polyisobutylenes based upon isobutylene. As already described isobutylene is one of the chief olefines obtained by cracking processes. This is the material used in the United States. In Germany isobutylene is obtained by passing gaseous hydrocarbons through the electric arc. It must also be remembered that the Germans have had large sources of petroleum derivatives available to them in recent years, chiefly from Rumania, but also from Austria.

According to Standard Oil Development Co.,[26] mono-olefines of 2, 3, and 4 carbon atoms form additional compounds with solid cuprous chloride and other cuprous halides, and it is shown that the dissociation temperature/pressure properties of these compounds quite sharply separate ethylene, propylene, and isobutylene from one another. Advantage of these properties is taken to separate the olefines from saturated hydrocarbons by forming the copper compounds at suitable temperature and pressure, isolating the mixture of copper compounds and dissociating it in stages at suitable temperatures and pressures to obtain each olefine in turn. If the cuprous halide is suspended in a saturated hydrocarbon of high boiling point, the speed of reaction is greatly increased, e.g. ethylene in contact with cuprous chloride at 25° C. and 17 atmospheres requires 24 hours for complete reaction, but in the presence of kerosene only 15 minutes.

Isobutylene may be polymerized by heating in the presence of catalysts such as aluminium chloride, boron chloride, stannic chloride, etc. Although it was found in 1873 by Butlerov and Gorianov[8] that isobutylene could be polymerized to a liquid product by means of sulphuric acid and/or boron fluoride as catalyst, it is only recently that rubbery products have been obtained, first by Otto and Mueller-Conradi.[21] Standard Oil Development Co. and I.G. Farbenindustrie[26] purified light cracked oil to give a mixture containing at least 95 per cent. isobutylene. Crude oil containing butanes and butylene was then added to produce a mixture containing from 20 to 40 per cent. of isobutylene, and 10 to 20 per cent. of other olefines. The mixture was then polymerized with boron fluoride at a temperature below − 40° C. to yield plastic solid or semi-solid rubbery materials. In another patent Standard Oil Development Co.[25] produced high molecular weight polymers of olefines, notably polyisobutylene, by passing the olefine into a bath of hydrocarbon diluent, such as ethane, propane, or butane, having an active catalyst, such as boron fluoride, and keeping

the temperature below -10° C. Isoprene, styrene, and butadiene could also be polymerized by this method. Polymerization occurred with the formation of substantially straight-line polymers. The nature of these varied with the molecular weight, ranging from oily viscous fluids up to strong rubbery materials with molecular weights as high as 500,000.

Jessup [18] has described how either or both of the straight chain chlorides or bromides of butane is heated in the presence of aluminium chloride, ferric chloride, or beryllium chloride at 300–500° C., when isobutylene is obtained.

The polyisobutylenes have already attained importance as commercial materials, being available as Oppanol made by I.G. Farbenindustrie, and as Vistanex made by Standard Oil Company.

German Production of Polyisobutylene.[32] Large-scale manufacture of polyisobutylene was carried out by the I.G. at Oppau. It was known as Oppanol. Maximum production had reached almost 5,000 tons per annum. Oppanol was designated as B. 8 to B. 250, corresponding to molecular weights of 8,000 and 250,000 respectively. Most widely used were Oppanols of between 50,000 and 200,000 molecular weights.

Isobutanol was made by high-pressure reaction between carbon monoxide and hydrogen. It was then catalytically dehydrated to isobutylene. It was then polymerized in liquid ethylene, using boron fluoride as catalyst at -80° to -100° C.

Isobutylene	1 part by weight
Ethylene	2 parts
Boron fluoride	0·001 to 0·003 parts

Production of Styrene. Styrene is second in importance only to butadiene, for enormous quantities are used as secondary component in the formation of elastomers such as Buna S. This is not only the predominant German type, but has been adopted as standard for United States production.

Actual production was 181,000 tons in 1945, 203,000 tons in 1946, and 155,000 tons in 1947.

It is prepared by a process first discovered by Berthelot,[1] namely the dehydrogenation of ethyl benzene. Ethyl benzene is obtained in small quantities as a by-product from petroleum refining and this source is being exploited in the United States. It is generally prepared by direct synthesis from benzene and ethyl chloride. Under the action of aluminium chloride as catalyst benzene and ethylene also combine to form ethyl benzene. This is catalytically dehydrogenated or cracked at high temperature, from 800–950° C. According to one process,

when carried out betweeen 500–600° C. over suitable catalyst, a yield of 35 per cent. is obtained.

Dow [10] has made an interesting comparison of existing methods of production of styrene, illustrating the advantages of the processes used by his company. He stated that in one method benzene and 95 per cent. alcohol were the starting materials being reacted at temperatures of about 600° F., and pressures of 250 lbs. per sq. in. over a phosphoric acid catalyst. In another method ethylene is used instead of alcohol. In both these cases very pure benzene is required. The benzene and ethylene must be recycled several times.

The Dow process can use impure ethylene containing as little as 38 per cent. of ethylene. Their operating temperature is only 190° F. at the low pressure of 15 lbs. per sq. in. The catalyst is aluminium

STYRENE FLOW CHART

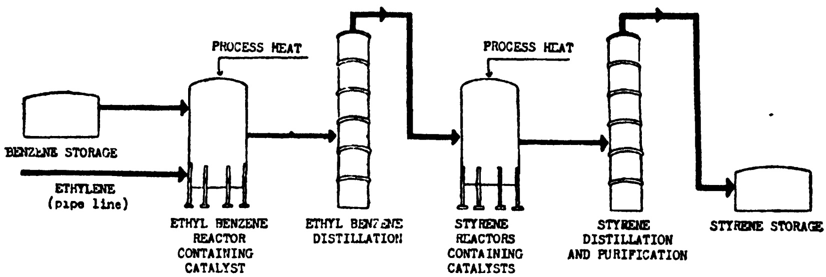


FIG. 25.

chloride, giving a yield of up to 100 lbs. of ethyl benzene per lb. of catalyst. A much lower grade of benzene could be used in this case. The reaction is carred out continuously, and gives almost theoretical yields of ethyl benzene. They can also recover about 80 per cent. of the spent aluminium chloride catalyst.

Benzene is, of course, obtained from coal tar, while ethyl chloride may be prepared via alcohol, or by the direct catalytic interaction of ethylene and hydrogen chloride.

Styrene is a colourless liquid with a characteristic pungent odour. It boils at 143° C., and has a density $d = 0{\cdot}904$.

The production of styrene in Germany has for many years been a major activity. As a primary ingredient of Buna S it was produced on a very large scale indeed. As a result, polystyrene has been a leading plastic, and very cheap.

Brown coal was the basic material. Benzene was obtained directly from this. Ethylene was obtained by dehydrogenating acetylene,

obtained from calcium carbide, obtained from brown coal. Benzene and ethylene were combined to form ethylbenzene, which was dehydrogenated to give styrene.[33]

Ethylbenzene was produced by reacting 98 per cent. ethylene and refined benzene in an enamelled steel tower at 90° C. in the presence of powdered aluminium chloride. The process was continuous and the stream leaving the reactor contained about 35 per cent. ethylbenzene, 50 per cent. benzene, and 15 per cent. higher alkyl benzenes. The ethyl benzene is separated by distillation. Yield on benzene

GERMAN PRODUCTION OF STYRENE

	Metric tons per month		
	Styrene	Polystyrene	Buna S
Ludwigshafen	1,000	500	2,000
Schkopau	1,700	50	6,000
Hüls	1,800		4,000
Auschwitz	1,000		3,000

95–96 per cent.; yield on ethylene 92–94 per cent.; 1 lb. of $AlCl_3$ is used up for about 40 lbs. of ethylbenzene. The two latter are recycled, returning to the reactor.

Ethylbenzene is dehydrogenated by passing over a special catalyst at temperatures of about 600° C. in the presence of steam. Ethylbenzene and steam in the ratio 1·1/1 is passed over catalyst in the form of $\frac{1}{8}$-inch rod, $\frac{1}{4}$ inch long. The furnaces consisted of bundles of 4-inch diameter tubes of copper-manganese coated steel, 8 feet long, filled with catalyst. The catalyst is composed of:

	Per cent.
Zinc oxide	80
Calcium oxide	5–7
Aluminium oxide	10
Potassium hydroxide	2–3
Chlorine oxide	0·5–0·7

It lasts about twelve months and gives an overall of 90 per cent. styrene. The liquid obtained by cooking the reaction gases comprises 40 per cent. styrene, 0·5 per cent. benzene, 1 per cent. toluene, a little tar and nearly 60 per cent. ethyl benzene. It is stabilized with 10 grams of hydroquinone per ton of solution and then redistilled. The pure styrene was controlled by continuous measurement of refractive index. (N_D^{20} 1·54669). It was stored in aluminium tanks under nitrogen.

Wakeman and Weil[29] have summarized the position.

With the current development of synthetic rubber, styrene as one of the components of Buna S, will become a large-tonnage chemical, a fact which will be reflected in increased production of polystyrene plastics in

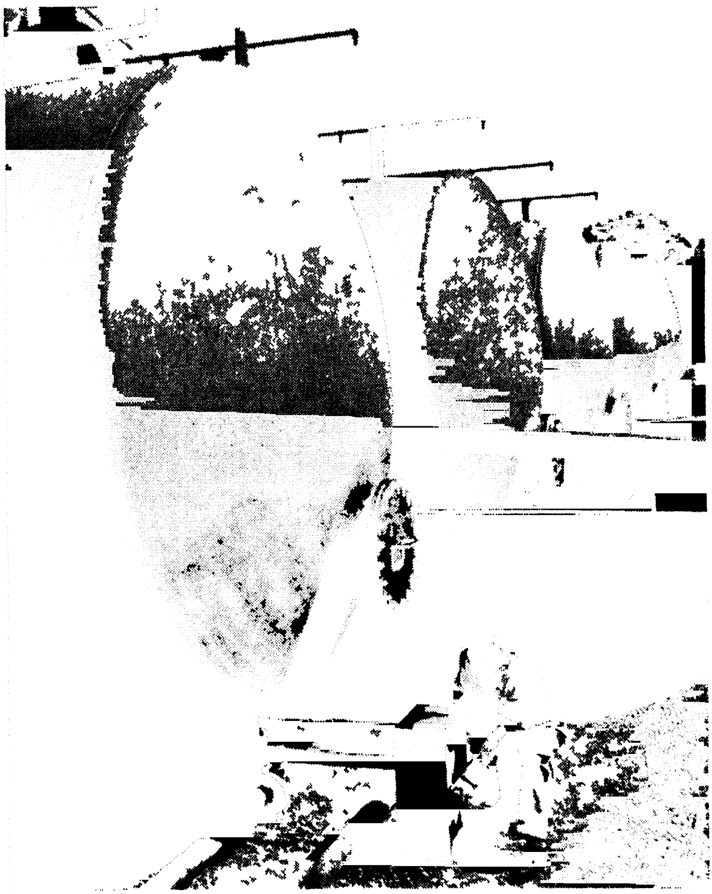


Fig 26—Styrene is stored in Tanks

moulded, extruded and film form. In Germany it is to-day one of the most available plastics and is utilized for many applications where cellulose acetate is used in the United States. It has been freely predicted that because of the increased production of styrene caused by the rubber industry, polystyrene will be one of the most available and least expensive plastics in this country after the present war.

In considering the production of styrene it becomes quite clear that despite all advances in petroleum technology the manufacture of synthetic rubber is still almost solely dependent on coal. Styrene is made from ethylene and benzene. It therefore hinges entirely on the availability of either ingredient. While ethylene is available from many sources, benzene is still almost wholly derived from coal. As yet there are no other commercial sources. Thus the 1946 production of GR-S required about 150,000 tons of styrene. This in turn required approximately 50 million gallons of benzene. When this is considered together with the rapidly mounting usage of polystyrene for plastics, almost one-half of all the benzene produced in the United States is utilized in styrene production.

Acrylic Acid Monomers. These are the secondary ingredients in such important products as Perbunan (containing acrylic nitrile), Hycar, Chemigum, and so on.

The group includes acrylic and methacrylic acids, their esters, halides, nitriles, etc. Polymers of many of these have already achieved considerable commercial importance as synthetic resins, notably methyl methacrylate (Lucite, Perspex, Plexiglas, etc.) and ethyl acrylate (Diakon, Plexiglas moulding powders).

$$CH_2{=}C\begin{matrix}\diagup COOH\\ \diagdown H\end{matrix} \qquad \text{acrylic acid}$$

$$CH_2{=}C\begin{matrix}\diagup COOH\\ \diagdown CH_3\end{matrix} \qquad \text{methacrylic acid}$$

The formation of acrylic acid esters conveniently starts from ethylene chlorohydrin. This is treated with sodium cyanide and yields ethylene cyanhydrin. When this is heated in the presence of sodium hydrogen sulphate, acrylic nitrile is formed, the most important derivative from the synthetic rubber angle.

$$\begin{matrix}CH_2\ OH\\ |\\ CH_2.Cl\end{matrix} + NaCN \rightarrow \begin{matrix}CH_2.OH\\ |\\ CH_2.CN\end{matrix} + NaCl$$

Ethylene chlorohydrin

$$\xrightarrow[\text{heat}]{KHSO_4} CH_2{=}C\begin{matrix}\diagup CN\\ \diagdown H\end{matrix}$$

Acrylic nitrile

Another method is the direct catalysed combination between ethylene oxide and hydrogen cyanide.

$$\begin{matrix} CH_2—CH_2 \\ \diagdown\ \ \diagup \\ O \end{matrix} + HCN \rightarrow CH - C\begin{matrix} \diagup H \\ \\ \diagdown CN \end{matrix} + H_2O$$

Another process employed in the United States proceeds according to the following reaction:

$$CH_3.COOCH_2.CH_2CN \xrightarrow{\text{heat}} CH_2\ \ C\begin{matrix} \diagup H \\ \\ \diagdown CN \end{matrix} + CH_3.COOH$$

Methyl methacrylate is derived fıom acetone, which, of course, can be obtained from acetylene. Acetone reacts with hydrogen cyanide to give acetone cyanhydrin. This is treated with sulphuric acid and methyl alcohol.

$$\underset{\text{Acetone cyanhydrin}}{\begin{matrix} CH_3 \diagdown & & \diagup OH \\ & C & \\ CH_3 \diagup & & \diagdown CN \end{matrix}} + H_2SO_4 + CH_3OH \rightarrow \underset{\text{Methyl methacrylate}}{CH_2{=}C\begin{matrix} \diagup COOCH_3 \\ \\ \diagdown CH_3 \end{matrix}} + NH_4HSO_4$$

Methyl methacrylate is a colourless liquid with a specific gravity at 16° C. of 0·9497 and refractive index n^{16}_{D} 1·4168. It boils at 100·3° C. It is soluble in most organic solvents, but is insoluble in water.

Acrylonitrile Preparation in Germany.[34] Acrylonitrile required for the manufacture of Perbunan-type synthetics was made by passing acetylene and dried hydrocyanic acid into a rubber-lined cylindrical tank, equipped with baffles and kept two-thirds full of the catalyst solution. The acetylene entered the reactor at three places in the bottom, and was redistributed by bells or jets. The hydrocyanic acid entered at the middle and at the bottom of the vessel, which was maintained at a temperature above 70° C. The acetylene and hydrocyanic acid were used in a molecular ratio of 10 to 1.

Acrylonitrile, together with acetylene and by-products, came off at the top of the vessel, and was washed with water into long columns to dissolve out the acrylonitrile and hydrocyanic acid, the remaining gases being returned to the reactor. The water solution was treated with direct steam in a second column, from which acrylonitrile at 80 per cent.

concentration was taken from the top. It was redistilled and fractionated in three columns equipped with shell and tube reboilers. The first freed the material from low-boiling compounds, the second (at 150 mm. vacuum) from high-boiling by-products. The third, also at

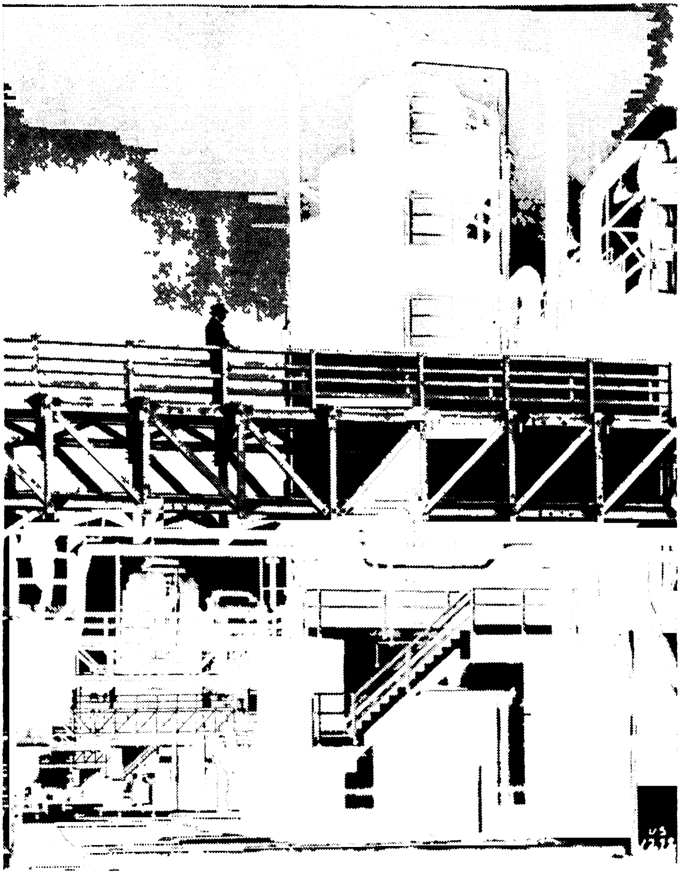


FIG 27—Monomer Recovery Plant

Here shown is a part of the recovery area where unreacted styrene is recovered and returned to storage at the co-polymer unit of the California Synthetic Rubber Project operated by United States Rubber Company at Los Angeles

150 mm. vacuum, redistilled these high-boiling by-products, any acrylonitrile passing back to the second. Acrylonitrile, 99 per cent. pure, was obtained from the head of the second column. The yield was 80 per cent. based on acetylene and 85 per cent. based on hydrocyanic acid.

A number of catalysts had been tried, but best results were found with the following two alternatives :

Material	Hüls	Ludwigshafen
Cuprous chloride . .	1,270 g.	1,485 g.
Water	1,200 g.	Make to 2,300 ml.
Sodium chloride . .	65 g.	175 g.
Potassium chloride .	860 g.	893 g.
	Make to pH 1 with HCl	

The catalyst was used for three weeks, and was then regenerated by precipitating the copper with wire and remaking to cuprous chloride.

Acrylic nitrile is a stable colourless liquid boiling at 77° C. and possessing a mild, pleasant odour.

It has a density of 0·8060 at 20° C. and refractive index $n^{20}{}_{D}$ 1·3911. It is soluble in all proportions in acetone, benzene, carbon tetrachloride, ether, alcohol, esters, and petroleum solvents. Its solubility in water at 20° C. is 3·1 per cent. It is somewhat toxic.

Some Costs. It is fascinating to consider some of the preliminary costings which were formulated at a very early stage. In view of the incredible success of the enormous projects these early costings are of the greatest educational value and interest. Fortunately sufficient data is available.

The Standard Oil Company [24] investigated the costs of producing butyl rubber and Buna S on a large scale. They considered four possible cases : the production of 100 tons per day, and 300 tons per day, of butyl rubber and Buna S respectively. They selected their best possible location of establishing such a project. The results of their study are summarized in the accompanying tables. One outstanding conclusion was that the costs of butyl rubber were extremely attractive, and that it was potentially the cheapest synthetic rubber. The production costs of Buna S were found to be something of the order of twice as great as those of butyl rubber. In connection with the estimate regarding butadiene, they selected a non-catalytic dehydrogenation method for making their estimate. They considered that in connection with the production of styrene for Buna S it would not be a difficult matter to prepare ethyl benzene by the alkylation of benzene, although the subsequent steps would present some difficulty. Of unusual interest is the fact that they also included information obtained from the I.G. in 1938 for their production of 73 tons of Buna S per day. The particulars given are of considerable interest as having a degree of authenticity which has hitherto been lacking.

TABLE 52. ESTIMATED COST OF BUTYL RUBBER—BAYTOWN [24]

(Plant of the Standard Oil Co.)

	Case I			Case II		
Quantities :						
Butyl rubber production, T/D		100			300	
Isobutylene consumed, lbs./D		212,000			636,000	
Butadiene ,, , lbs./D		10,000			30,000	
Normal Butane ,, , B.P.D.		1,550			4,650	
Investments :						
Isobutylene		$4,400,000			$10,500,000	
Butadiene		750,000			2,200,000	
Butyl rubber		4,650,000			11,100,000	
Total incl. 25% for offsite		$9,800,000			$23,800,000	
Production cost, $/day :						
Isobutylene	at 3·1 c.	$6,500	3·3 c.	at 2·7 c.	$17,300	2·9 c.
Butadiene	at 12·2 c.	1,200	9·6 c.	at 9·2 c.	2,800	0·5
Butyl rubber		7,300	3·6		19,300	3·2
Total		$15,000			$29,400	
c./lb. butyl rubber			7·5 c.			6.6 c.
Increase in c./lb. butyl rubber for a $1/bbl. increase in normal butane			0·78 c.			0·78 c.

TABLE 53. ESTIMATED COST OF BUNA-S MANUFACTURE—BAYTOWN [24]

	Case III			Case IV		
Quantities :						
Buna-S production, T/D		100			300	
Butadiene consumed, lbs./D		165,000			495,000	
Styrene ,, , lbs./D		50,000			150,000	
Stabilizer gas ,, , MCFD		0·48			1·45	
Normal butane ,, , BPD		2,400			7,200	
Benzol, gals./D		7,000			21,000	
Investments :						
Butadiene		$9,600,000			$23,300,000	
Styrene		3,550,000			8,300,000	
Buna-S plant		7,500,000			18,000,000	
Total, incl. offsite at 25%		$20,650,000			$49,600,000	
Production cost, $/day :						
Butadiene	at 8·6 c.	$14,200	7·1 c.	at 7·9 c.	$39,200	6·5 c.
Styrene	at 11·4 c.	5,700	2·9 .	at 9·5 c.	14,300	2·4
Buna processing cost, ex chemicals		6,000	3·0		15,000	2·5
Chemicals for Buna processing		6,000	3·0		18,000	3·0
Total		$31,900			$86,500	
c./lb. Buna			16·0 c.			14·4 c.
Increase in c./lb. Buna S for a $1/bbl. increase in normal butane			1·20 c.			1·20 c.

Table 54. Estimated Cost of Isobutylene for Butyl Rubber Manufacture—Baytown [24]

	Case I		Case II	
Quantities :				
Butyl rubber produced, T/D	100		300	
Pure isobutylene „ , lbs./D	212,000		636,000	
Isobutane „	—		—	
N-butane consumed, BPD	1,550		4,650	
Investments :				
Fractionation of field butane	$ 0		$ 0	
Isomerization and fractionation	750,000		1,800,000	
Catalytic dehydrogenation	1,700,000		4,100,000	
Isobutylene concentration (H_2SO_4 process)	1,050,000		2,500,000	
Total	3,500,000		8,400,000	
Offsite at 25%	900,000		2,100,000	
Total	$4,400,000		$10,500,000	
Processing costs, $/day :				
Fractionation of field butane	$ 0	0 c.	$ 0	0 c.
Isomerization and fractionation	1,500	0·71	3,600	0·57
Catalytic dehydrogenation	2,200	1·04	6,000	0·94
Isobutylene concentration	1,700	0·80	4,400	0·69
Total	5,400	2·55	14,000	2·20
N-butane cut at 70 c./B	1,100	0·52	3,300	0·52
Total	6,500		17,300	
Isobutylene cost, c./lb. with *n*-butane at 70 c./bbl.		3·1 c.		2·7 c.
„ „ „ „ „ „ $1.70/bbl.		3·8 c.		3·4 c.

Table 55. Estimated Cost of Butadiene for Butyl Rubber–Baytown [24]

	Case I	Case II
Quantities :		
Butyl rubber produced, T/D	100	300
Butadiene „ , T/D	5	15
Concentrated butylenes, lbs./D	22,000 [a]	65,500 [b]
Investments :		
Butylene concentration	$ 0	$ 450,000
Butylene cracking and butadiene concentration	600,000	1,300,000
	600,000	1,750,000
Offsite	150,000	450,000
	$750,000	$2,200,000
Processing Costs :	(cents)	(cents)
Butylene concentration	0	1·4
Butylene cracking and butadiene concentration	10	5·6
	10	7·0
Butylene raw material at 1·0 c./lb. (value for U. O. P. polymer + frt.)	2·2	at 1·0 c.[c] 2·2
c./lb. Butadiene	12·2	9·2

[a] From Baton Rouge V. P. cracking plant.
[b] ½ from B.R. cracking plant (34,200 lb./CD N. C_4H_8 in C_4 cut) and ½ from Baytown spent C_4 from codimer plant.
[c] Value for alkylation.

TABLE 56. ESTIMATED COST OF BUTADIENE FOR BUNA-S MANUFACTURE—BAYTOWN [24]

	Case III		Case IV	
Quantities :				
Buna-S produced, T/D	100		300	
Pure butadiene produced, lbs./D	165,000		495,000	
N-butane consumed, BPD	2,400		7,200	
Investments :				
Fractionation of field butane	$ 0		$ 0	
Catalytic dehydrogenation	2,600,000		6,300,000	
Butylene concentration (H_2SO_4 process)	1,700,000		4,100,000	
Butylene cracking (non-catalytic)	1,800,000		4,300,000	
Butadiene concentration (Cu process)	1,600,000		3,900,000	
	7,700,000		18,600,000	
Offsite at 25%	1,900,000		4,700,000	
Total	9,600,000		23,300,000	
Processing costs, $/day :				
Fractionation of field butane	$ 0	0c.	$ 0	0c.
Catalytic dehydrogenation	3,800	2·3	10,300	2·1
Butylene concentration	2,900	1·8	7,500	1·5
Butylene cracking	3,000	1·8	8,400	1·7
Butadiene concentration	2,800	1·7	7,900	1·6
Total	12,500	7·6	34,100	6·9
N-butane at 70 c./bbl.	1,700	1·0	5,100	1·0
	14,200		39,200	
Butadiene cost, c/lb. with n-butane at 70 c./bbl.		8·6 c.		7·9 c.
Butadiene cost, c./lb. with n-butane at $1.70/bbl.		10·1 c.		9·4 c.

TABLE 57. ESTIMATED COST OF STYRENE FOR BUNA-S MANUFACTURE—BAYTOWN [24]

	Case III			Case IV		
Quantities :						
Buna-S production, T/D		100			300	
Styrene production, lbs /D		50,000			150,000	
Benzene consumed, gals./D		7,000			21,000	
Ethylene consumed, lbs./D		18,700			56,100	
Stabilizer gas consumed, MCF		0·48			1·45	
Investments :						
Propane cracking and Ethylene fractionation		$ 700,000			$1,500,000	
Ethyl benzene manufacture		650,000			1,500,000	
Styrene manufacture		1,500,000			3,600,000	
		2,850,000			6,600,000	
Offsite at 25%		700,000			1,700,000	
		3,550,000			8,300,000	
Processing costs, $/day :						
Ethylene manufacture	at 4·3 c./lb.	$ 800	1·6 c.	at 2·9 c./lb.	$1,600	1·1 c.
Ethyl benzene manufacture		1,300	2·6		2,600	1·7
Styrene manufacture		2,500	5·0		6,800	4·5
		4,600	9·2		11,000	7·3
Benzene raw material at 16 c./gal.		1,100	2·2		3,300	2·2
		$5,700			$14,300	
c./lb. styrene						9·5 c.

TABLE 58. ESTIMATED YIELDS[24]

Butyl rubber:

1. 98% normal butane to 98% isobutane by alkylation, incl. fractionation	95% of theory
2. 98% isobutane to *net* dilute isobutylene, by catalytic dehydrogenation	80% of theory
3. Net dilute isobutylene to pure isobutylene, by regeneration from H_2SO_4	95% of theory
4. 1·06 lbs. pure isobutylene/lb. butyl rubber 0·05 lb. ,, butadiene / ,, ,, ,,	

$$\frac{1{\cdot}06 \times 58}{4{\cdot}86 \times 56 \times 0{\cdot}95 \times 0{\cdot}80 \times 0{\cdot}95 \times 0{\cdot}98} = 0{\cdot}320 \text{ gals. 98\% normal butane cut/lb. butyl rubber}$$

Buna-S:

1. 98% normal butane to net dilute *n*-butylenes, by catalytic dehydrogenation	80% of theory
2. Net dilute *n*-butylenes to pure *n*-butylenes, by regeneration from H_2SO_4	95% of theory
3. Pure *n*-butylenes to net dilute butadiene, by thermal cracking	50% of theory
4. Net dilute butadiene to pure butadiene, by cuprous salt extraction	95% of theory
5. 0·825 lb. butadiene/lb. Buna-S 0·250 lb. styrene /lb. ,, ,, (0·035 gal. benzol /lb. ,, ,,) (0·0935 lb. ethylene/lb. ,, ,,) (2·4 CF stabilizer gas/lb. Buna-S)	

$$\frac{0{\cdot}825 \times 58}{4{\cdot}86 \times 54 \times 0{\cdot}80 \times 0{\cdot}95 \times 0{\cdot}50 \times 0{\cdot}95 \times 0{\cdot}98} = 0{\cdot}516 \text{ gals. 98\% normal butane cut/lb. Buna-S}$$

TABLE 59. I.G. COST ESTIMATE (DEC. 1938) FOR 73 TONS BUNA-S/DAY (2,000 MT/MO)[24]

	(dollars)
Investment:	
Butadiene (chlorination process)	6,500,000
Styrene	900,000
Polymerization	5,000,000
Other, in battery limits	2,600,000
	15,000,000
Offsite	5,000,000
	20,000,000
	(cents)
Production Cost:	
Butadiene at 10·5 cents	8·4
Styrene at 13·4 cents	3·5
Buna processing cost, ex chemicals	3·7
Chemicals for Buna processing	2·9
cents per lb. Buna-S	18·5

An estimate of butyl rubber costs for a production of 20 tons per day at their Baton Rouge plant was made by Standard Oil Development Co.

The fact that the total cost of alcohol-rubber has proved to be far higher than that of petroleum-rubber is mainly, if not wholly, due to the difference in the prices of the two basic materials, alcohol and petroleum (or natural gas) fractions. The original cost estimates for alcohol-rubber were based on the opinion of the experts that alcohol could probably be purchased for about 50 cents per gallon, and their estimates showed that even at that price the cost of alcohol-rubber would be much higher than that of petroleum-rubber. As a matter of fact, the average price paid by the synthetic-rubber industry for alcohol during 1944 averaged more than 90 cents per gallon, with a resultant total cost for the alcohol-rubber far higher than it would have been if alcohol could have been obtained for 50 cents.

TABLE 60. BUTYL RUBBER COSTS (20 TONS PER DAY)

	c./lb. of butyl rubber
Raw material:	
Isobutylene, at 7·76 c./gal.	1·70
Isoprene, at 30 c./oz.	1·20
Operating costs:	
Operating labour and supervision (approximately 26 men per shift)	2·17
Maintenance:	
Normal	2·01
Changes and additions	1·55
Utilities:	
Fuel-free	0·46
Fuel, at 12 c./MM B.T.U.	0·86
Chemicals:	
Methyl chloride	0·35
Aluminium chloride	0·30
Other chemicals	0·49
Total	1·25
Other supplies	0·12
Burden and administrative and general expenses	3·18
Containers	0·71
Total, excluding royalty, depreciation, profit	15·21
Say	15·00

The following tabulation compares the preliminary cost estimates for GR-S rubber with the actual results (not entirely complete in their coverage) during the month of May 1944. The figures include provision for amortization of the investment over a period of five years, but not for interest on investment or for selling expenses. Costs were

also computed to include amortization over a period of ten years and also with no provision for amortization.

Since much more butadiene is used than styrene, the largest factor in the cost of GR-S, whether made from alcohol or from petroleum, is that of butadiene. The next largest element in cost is that of copolymerization, which is, of course, independent of the cost of the constituent materials. Styrene is a relatively minor factor.

The original estimates for alcohol-rubber were based on a price of 50 cents per gallon. Corresponding estimates based on 95 cents, and 15 cents, per gallon, respectively, have been computed from the same data by the Tariff Commission.

TABLE 61

(In cents per pound of Rubber)

	Butadiene	Styrene	Copolymerization	Total
Alcohol process with price of alcohol:				
95 cents per gallon: [a]				
Based on advance estimate	37·1	4·6	7·9	49·6
Actual, May 1944	35·7	4·8	7·4	47·9
50 cents per gallon:				
Advance estimate	22·0	3·5	7·9	33·4
Actual [b]	20·6	3·8	7·4	31·7
15 cents per gallon:				
Based on advance estimate	10·4	2·6	7·9	20·9
Actual [b]	8·8	2·9	7·4	19·1
Butene-butane (petroleum) process:				
Advance estimate	8·1	2·3	7·9	18·3
Actual	12·7	2·4	7·4	22·5

[a] The Actual price paid by the plants has been over 90 cents per gallon in 1944.

[b] That is to say, what the actual costs would have been if alcohol could have been bought at 50 cents, or 15 cents, per gallon respectively.

The preliminary estimates placed the cost of copolymerization at 7·9 cents per lb. of rubber; the actual experience during May 1944 showed a slightly lower figure, 7·4 cents. On the basis of an alcohol price of 95 cents per gallon (approximately the actual price during most of 1944), the advance estimate of the experts would have shown the cost of alcohol-butadiene required for a pound of rubber as 37·1 cents; the actual cost, calculated on 95-cent alcohol, during May 1944, proved to be 35·7 cents. The advance estimate placed the cost of petroleum-

butadiene required for a pound of rubber at 8·1 cents; the actual cost proved to be 12·7 cents, but even this figure was only about one-third of the cost of alcohol-butadiene based on a 95-cent price for alcohol.

Combining the cost of styrene with the other two factors, the advance estimate for the total cost of alcohol-rubber, if it had been based on alcohol at 95 cents per gallon, would have amounted to 49·6 cents, whereas the actual cost proved to be a little less than 48 cents. The advance estimate of the total cost of the petroleum-rubber was 18·3 cents, whereas the actual figure in May 1944 proved to be 22·5 cents; it is probable, however, that if the plants making butadiene from petroleum had been in full operation at that time the total cost would have approached the lower preliminary estimate. Even under the actual conditions of operation during that month the total cost of petroleum-rubber was less than half the cost of alcohol-rubber based on a price of 95 cents per gallon for alcohol, which corresponded approximately to the actual price paid. Even if it had been found possible to buy alcohol at 50 cents per gallon, the cost of the alcohol-rubber in May 1944 would have been more than one-third higher than that of petroleum-rubber.

It appears also from the above table that only if the price of alcohol had fallen to around 15 cents per gallon would the cost of alcohol-rubber have been in the same range with that of petroleum-rubber.

This analysis becomes rather academic in view of the current world shortage of cereals and foodstuffs. There seems little likelihood of any vast quantities of alcohol from cereals for many years. Even less likely is low-price alcohol. The high price of cereals puts this completely beyond the realms of possibility.

A price of 15 cents per gallon would be little more than half of the average price of alcohol during the pre-war period, when it was being made chiefly from molasses, a much cheaper material than grain, which has had to be the principal material for the greatly increased output of alcohol necessitated by the rubber programme.

In 1948 Hale has claimed that alcohol can be made by a new process from grain at 25 cents per gallon which gives butadiene at 8 cents.

The costs shown in the above tabulation are based on amortization of investment in five years. If amortization were spread over ten years the average costs of production of GR-S rubber, whether made from alcohol or from petroleum as a base, would average between 2 and 3 cents per lb. lower than those shown in this tabulation. Similarly, if there were no provision for amortization the average costs would be between 5 and 6 cents per lb. lower than shown in the tabulation.

One factor which may affect the post-war competition of synthetic

with natural rubber is the relative costs of the processes involved in making tyres from these two kinds of rubber. Up to the present time the processing of GR-S rubber, if used alone, has been more costly than that of natural rubber, though the difference is less if natural is mixed with the synthetic. Further improvements in the qualities of GR-S (or of other synthetic rubbers), or in the methods of manufacturing tyres from it, may reduce or even in time eliminate, the excess in tyre-processing costs.

REFERENCES

[1] BERTHELOT, *Bull. Soc. Chim* , 1866, **6**, 296.
[2] BOYD, *Ind. Eng. Chem.*, 1941, **33**, 324.
[3] BROOKS, U.S.P. 1,988,479/1935.
[4] BROOKS and ELLIS, *Science of Petroleum*, Oxford Univ. Press, 1939, p. 2806.
[5] BROUS, U.S.P. 2,041,814/1936.
[6] BURTON, U.S.P. 1,049,667/1912.
[7] Butadiene Storage—*Chem. Met. Eng.*, 1942, **49**, 118.
[8] BUTLEROV and GORIANOV, *Ann.*, 1873, **169**, 146.
[9] CRAMER, *Ind. Eng. Chem.*, 1942, **44**, 243.
[10] Dow Chemical Co., B.P., 526,387/1940.
[11] DOW, *Ind. Eng. Chem.*, 1942, **34**, 1267.
[12] DUNSTAN, *Chemistry and the Petroleum Industry*, 1942, p. 20.
[13] ELDER, *Ind. Eng. Chem.*, 1942, **34**, 1260.
[14] FREY and HEPP, *Science of Petroleum*, Oxford Univ. Press, 1939, p. 1994.
[15] FRÖLICH, *Ind. Eng. Chem.*, 1940, **32**, 293.
[16] GROSSE and IPATIEFF, *Ind. Chem. Eng.*, 1940, **32**, 268.
[17] GROSSE, MORRELL and MAVITY, *Ind. Eng. Chem.*, 1940, **32**, 309
[18] JESSUP, B.P. 536,734/1941.
[19] KHARASCH, *Ind. Eng. Chem.*, 1947, **39**, 831.
[20] KOLACHOV, *Chem. Eng. News*, 1943, **21**, 488.
[21] LEBEDEV, *Zhizn. i Trudni* (Moscow), p. 471.
[22] OTTO and MUELLER CONRADI, U.S.P. 2,130,507/1938.
[23] SCHULZE and SCHULZE, *Kautschuk*, 1939, **15**, 182.
[24] Standard and I.G., *Fortune*, August 1940, p. 119.
[25] Standard Oil Company, *U.S. Committee on Patents*, Part 6, p. 3052.
[26] —— *ibid.*, p. 3119.
[27] Standard Oil Development Co., and I.G., B.P. 407,932/1937.
[28] Standard Oil Development Co., B P. 537,497/1940.
[29] —— B.P. 483,453/1938.
[30] WAKEMAN and WEIL, *Ind. Eng. Chem.*, 1942, **34**, 1387.
[31] WEIZMANN, BERGMANN and KIND, B.P. 552,216 ; B.P. 552,115 ; B.P. 573,383.
[32] C.I.O.S., XXIII–15.
[33] C.I.O.S., XXII–21.
[34] C.I.O.S., XXIII–25.

CHAPTER 8

POLYMERIZATION

Polymerization a Major Problem in the Production of Synthetic Rubber. The production of the primary materials for making synthetic rubbers appears to be streamlining to a cheap and simple procedure. Vast quantities of olefines, diolefines, and their derivatives are being obtained from plentiful cheap raw materials such as coal, petroleum, lime, salt, and so on. It is equally important that conversion of these materials into the final synthetic rubbers should also be smooth and easy, and should yield regular homogeneous products. The process of polymerization has proved just as difficult a problem as the production of raw materials.

Examples of the polymerization process described in the historical introduction make it evident that the procedure was invariably laborious, lengthy, and usually resulted in unsatisfactory materials. Synthetic rubber production has run the whole gamut of polymerization processes. One of the major fields for polymerization, it has greatly contributed to its development in other directions, in many other industries. For example, there has been a very notable contact between activities to produce synthetic rubbers and those directed at making synthetic resins. That is why producers interested in the one are almost invariably equally interested in the other form of production.

The academic work on raw rubber has all along provided the background for the production of synthetic resins; but even the work on rubber was merely a continuation of still earlier work. For example, polymerization action has been known for a very long time, certainly for 100 years. Thus Regnault[32] described the production of vinylidene chloride as long ago as 1838, although the first commercial materials known as Saran have only recently made their appearance. There was a considerable amount of similar empirical work prior to the first systematic efforts with natural rubber. The profound contributions of Harries, and his contemporaries, as a preliminary to the production of synthetic rubber has already been discussed.

The Polymerization Process. A monomer is a chemical entity such as styrene, vinyl chloride, vinyl acetate, methyl methacrylate, and so on, in the vinyl series, or such as butadiene, isoprene, chloroprene, etc., in the diolefine (or divinyl) series.

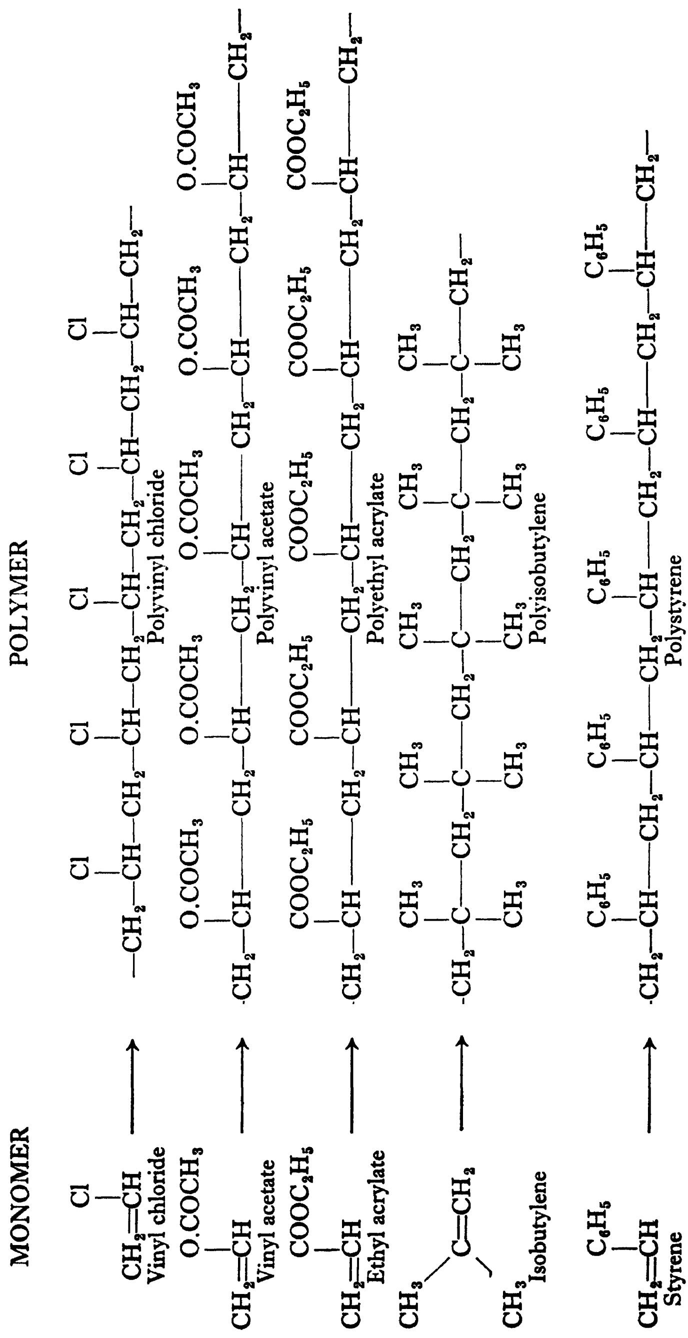


FIG. 28.—Monofunctional Monomers and their Polymers.

Polymerization is generally regarded as the linking up of a number of these monomeric units into long open chains or macro-molecules. This is the Staudinger conception, which is widely accepted. Each monomer unit forms a link in a straight uninterrupted chain. According to the treatment and the conditions, it is thought that chains of various lengths are formed. The properties of the product depend upon the extent to which polymerization is carried out, or, in other words, to the length of the chain. The molecular weight (generally determined by the viscosity) of the product gives the measure of the degree of polymerization. As the length of the polymer increases so the valuable mechanical properties become more apparent.

The character of the material changes, generally from the liquid state, since most monomers are liquids. These become more viscous, and then perceptibly change over towards the solid state. The various monomeric butadiene derivatives change to rubbery solids, and so on. Liquid styrene ultimately changes to the solid, glassy polystyrene, having remarkable electrical properties. Gaseous vinyl chloride which actually boils at $-14°$ C. forms the tough, strong polyvinyl chloride. Ethyl acrylate becomes a somewhat soft glassy solid, flexible, but having exceptional mechanical strength. Methyl methacrylate polymerizes to much harder transparent solids, which have remarkable light transmission. The straight chains initially formed by polymerization may tend to become cyclized by linking along the chain.

During the last twenty years, a vast amount of work has been carried out on polymerization notably by Staudinger,[37] Carothers,[5] Mark,[24] Whitby,[42] Marvel,[26] Flory and their colleagues.

Structure of Polymers. All the work carried out by these authorities almost unanimously leads to the conclusion that high polymers generally, whether natural or synthetic, are made up of enormous molecules containing hundreds of thousands of atoms bound together. There seems general agreement that many naturally high polymers such as rubber, cellulose, silk, etc., have a long molecule in the form of a long chain or thread. It seems likely also that in these materials the number of cross linkings between adjacent long molecules is very small. The term cross linking refers to straight chains or branch chains which have more than one main valency bridge between them. There is a great weight of evidence also that many other polymers which come into the study of synthetic rubbers such as polyisobutylene, polyacrylic esters, polystyrene, polyvinyl acetate, etc., also have these long-chain threadlike molecules, especially when they have been produced at low temperatures. Branching refers to long-chain molecules which branch as one proceeds along the molecule. So that

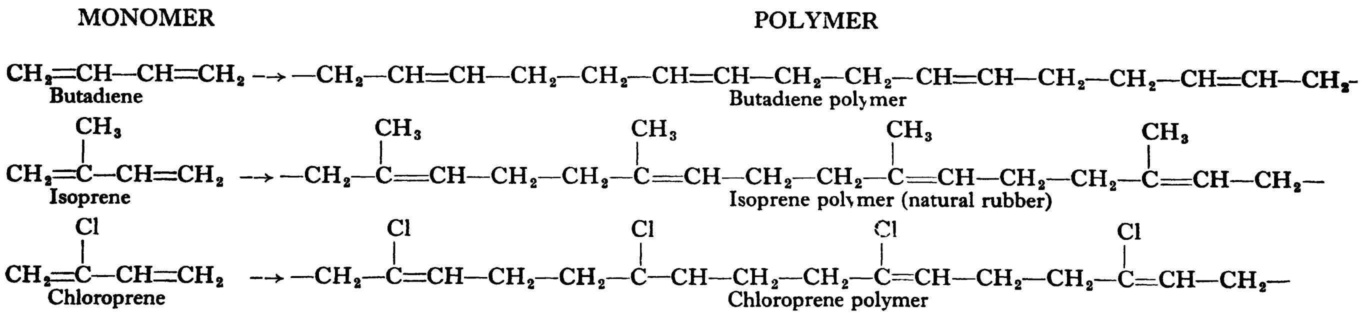
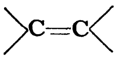
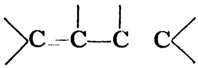
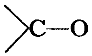
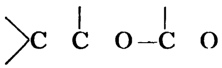
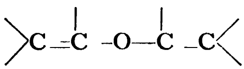
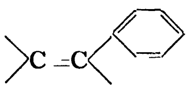
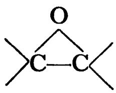
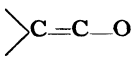


FIG 29 —Bifunctional Monomers and their Polymers

starting off with a single linear structure, this branches into two or more straight chains each of which in turn may branch, and so on. This type is more frequently encountered with multi-functional polymers. In addition to these types of polymers, there are also those known as net and space polymers, which are 2- or 3-dimensional.

The general behaviour of these types of materials show very clearly defined differences. These have been summarized by Mark and Rath.[25]

TABLE 62. ATOMIC GROUPS WHICH PARTICULARLY FAVOUR POLYMERIZATION (Thompson)[39]

Group	Compound
	Ethylene, vinyl chloride
	Butadiene, chloroprene
	Aldehydes
	Vinylacetate
	Divinylether
	Styrene
	Ethylene oxide
	Ketene

Thus the 2- or 3-dimensional polymers usually swell to a limited extent and do not go into solution. Examples of these are vulcanized rubber, Perbunan, neoprene, etc. They have no definite softening zone of temperatures. They tend to become plastic only at relatively high temperature, and then decompose slowly; a breakdown which is accompanied by increasing plasticity. They exhibit much greater resistance to abrasion and impact and heat than do the long-chain polymers. If there are many cross linkages, they become brittle and

lose their elasticity. They are also found to give very indistinct ring amorphous X-ray diagrams.

In the actual polymerization there are two main directions for the process. One can either produce straight-chain polymers, or alternatively, cyclized polymers, while combinations of these are also possible. It is generally accepted that straight-chain products will process easily, and if subsequent vulcanization or setting is not impeded, then probably such products are most desirable. Cyclized materials are much

FIG. 30.—Polymerization takes place in Large Glass-lined Vessels called Reactors at the Institute Plant, West Virginia

less readily processed, possibly owing to steric hindrance. In any event, the great problem is to make the polymerization process steer a regular well-defined course.

It is generally considered that in the production of synthetic high polymers the straightforward chain polymers are predominantly formed in those cases where the monomeric material contains only one polymerizable group, i.e. a double or triple bond. Outstanding examples of such monomers are vinyl chloride, vinyl acetate, acrylic acid ester, isobutylene, etc. These are the materials which Carothers called *mono-functional* (see Fig. 28).

In the case of most synthetic rubbers the reacting monomer is one which contains two or more reactive groups, such as butadiene, isoprene, chloroprene, etc. In these cases the formation of 2- or 3-dimension

TABLE 63. COMPARISON OF THE RATES OF POLYMERIZATION OF HYDROCARBONS DIFFERING ONLY IN THE AMOUNT OF UNSATURATION.[36]

Compound	Percentage conversion under given conditions
Butene-1 $CH_2{=}CH{-}CH_2CH_3$	39·6% in 52·5 seconds at 750° C. Stable at 200° C.
Butadiene-1,3 $CH_2{=}CH{-}CH{=}CH_2$	10 days at 150° C. in sealed tube, all polymerized. 70% polymerized in one hour at 350° C.
Vinylacetylene $CH{\equiv}C{-}CH{=}CH_2$	Explosive polymerization on contact with sulphuric acid or upon heating. Under pressure readily polymerized to a solid. Homologues form viscous syrups upon standing for two or three months.
Diacetylene or Butadyn $CH{\equiv}C{-}C{\equiv}CH$	Explodes at 35°. Definite polymerization in 5 minutes at 0° C.

polymers is not only possible, but usually takes place. These are the monomeric materials which Carothers called *bi-functional*, or *multi-functional* (see Fig. 29).

It is interesting to observe that these modern conceptions of the formation of polymers no longer find it necessary to use the idea of

TABLE 64. INFLUENCE OF CONJUGATION ON POLYMERIZATION[36]

Substance	Formula	Polymerization
Diacetylene	$CH{\equiv}C{-}C{\equiv}CH$	Polymerizes extremely rapidly
Divinylacetylene	$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$	Polymerizes rapidly
Vinylacetylene	$CH{\equiv}C{-}CH{=}CH_2$	Polymerizes very readily
Butadiene-1.3	$CH_2{=}CH{-}CH{=}CH_2$	Polymerizes readily
Pentadiene-1,4	$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$	Rearranges into the conjugated system and polymerizes readily
Hexadiene-1,5	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$	Polymerizes slowly

partial valencies which was the essential feature of Thiele's theory,[41] and on which many of the earlier ideas were based. Particularly in connection with rubber-like polymers it is important to notice the part played by a conjugated system of double bonds.

In the case of butadiene and its homologues on which most synthetic rubber work has been based, it soon became evident that substitution in the butadiene molecule had a profound effect on the rate of polymerization, and on the nature of the product formed. Lebedev[23] first showed that 1-phenyl-1,3-butadiene polymerized much more rapidly at 150° C. than did isoprene, which in turn polymerized much faster

TABLE 65. RELATIVE SPEEDS OF POLYMERIZATION OF VARIOUS DIENES COMPARED WITH ISOPRENE

(According to Carothers)
Temperature 25° C.

Compound	Position and nature of substituent C 1	C 2	C 3	C 4	Estimated speed	Character of polymer
1	--	Cl	Cl	-	2000	Hard, not extensible
2	-	I	-		1500	Rubber-like under certain conditions
3	—	Br	--		1000	Good rubber
4		Cl	—	—	700	Excellent rubber
5		Cl	CH_3	—	500	Fair rubber, but low extensibility
6	Cl	Cl	Cl	—	120	Soft, elastic
7	--	C_6H_5	-	—	90	Soft
8	CH_3	Cl	—	--	30	Soft
9	C_2H_5	Cl	-	—	30	Soft
10	C_4H_9	Cl	—	—	10	Soft
11	C_7H_{15}	Cl	—	—	10	Soft
12		C_7H_{15}	-	—	9	Soft
13	Cl	--	—	—	7	Soft, sticky
14	—	CH_3	CH_3	--	3	Fair rubber, but low extensibility
15	CH_3	CH_3	Cl	—	1·5	Soft
16	—	CH_3	—	—	1·0	Fair rubber
17	--	—	—	—	0·8	Fair rubber

than 1-methyl-1,3-butadiene. Whitby and Gallay[44] showed that the ability of a conjugated diolefine to form synthetic rubber required the presence of three hydrogen atoms on the end carbons of the molecule. Their extensive investigations showed that terminal substitution and increase in the degree of substitution both retard polymerization.

Carothers has carried out comprehensive investigations of the influence of substituting halogens in butadiene.[6, 7, 8] His results are summarized in Table 65.

Methods of Polymerization. Polymerization is generally achieved by four main methods, namely:

1. Direct polymerization of the monomer without a solvent.
2. Polymerization of the monomer in some solvent.
3. Polymerization of the monomer dispersed in some immiscible solvent.
4. Polymerization in the gaseous phase.

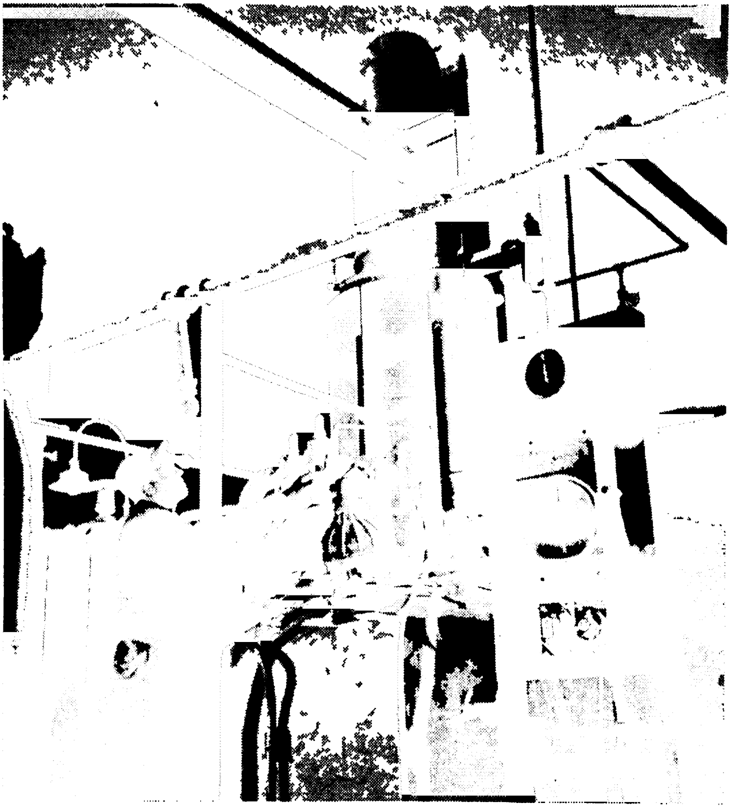


FIG. 31.—Another View of a Polymerization Reactor.

The medium plays a very important rôle in the polymerization.

The first two types are both single phase, the systems being homogeneous liquids. The first method is still widely used in the production of synthetic resins, for example, in the polymerization of styrene and methacrylic ester. The second method involving solvents is employed with vinyl chloride, styrene, and so on. Normally these processes are carried out at moderate temperatures up to 150° C., and at ordinary

pressure. With isobutylene very low temperatures are customary. In some cases, notably ethylene, high pressures are employed.

For many years the first two methods were predominant, but recently the third type of procedure has overshadowed the others and seems destined to supersede them. It is usually referred to as emulsion polymerization, because the immiscible solvent is generally water, and consequently since most monomers are liquids, emulsions are formed. Moreover, with adequate precautions such as the presence of a protective colloid, the final product remains in the dispersed form, either as an emulsion, or dispersion, according to whether the polymer is liquid or solid.

In some instances as, for example, vinyl acetate, the monomer is soluble in water, and thus represents the second type of polymerization. As polymerization proceeds, the product may be insoluble in water, in which case this forms a dispersion, and the subsequent action is once again that of emulsion polymerization.

The method adopted to carry out polymerization has a profound effect on the properties of the ultimate product. Staudinger and Frost[38] have effectively demonstrated this by the work on the polymers obtained from styrene. They found that polymerization in emulsion was much more rapid than polymerization of pure styrene. The variations in molecular weights of the polymers were considerable, as shown in Table 66.

TABLE 66. VARIATIONS IN MOLECULAR WEIGHT OF POLYMERS PRODUCED BY DIFFERENT POLYMERIZATION METHODS

Temperature of polymerization of styrene, ° C	Molecular weights of polymers	
	From pure styrene	From styrene in emulsion
30	600,000	750,000
60	350,000	400,000
100	120,000	175,000

When the commercial materials are considered, namely, the synthetic elastomers and the ethenoid plastics, it becomes quite evident that the most important method of production at the present time is that of emulsion polymerization. Most large manufacture is based on this process. It also represents the most outstanding trend in plastics production at the present time. It brings in its train another very important trend, namely, the production of synthetic rubbers by

continuous process. It heralds the transition from batch production to continuous production.

The other leading method for the production of synthetic rubber involves the use of sodium as promoting agent. This was the process developed before the last war. It is still used for the minor German production such as Buna 85 and Plastikator 32. For Buna S they have now abandoned this method of polymerization in favour of emulsion polymerization.

According to Ziegler [49] the particular advantage of polymerization with sodium is the use of a concentrated system while the disadvantage is the difficulty of dissipating the considerable heat of polymerization. The properties of the polymers, using the viscosity of a solution as the criterion, can be controlled by addition of specific reagents during polymerization and various products can thus be made. The outstanding user of the sodium process has always been the U.S.S.R. which has specialized in it. They still carry out very large-scale manufacture using the sodium method, although they also have an increasing production based on the emulsion process. The advantages of emulsions are the complete control over heat of polymerization, availability of the product as a latex, and the facilities to form copolymers. Another advantage is the enormous increase in scope afforded.

Heat Polymerization. It was observed quite early that isoprene and dimethylbutadiene underwent spontaneous polymerization to rubber-like products when kept for a long period at room temperature. From this it was only a short step to the discovery that the polymerization of the dienes could be brought about more quickly by the application of heat. The polymerization of isoprene by heat was patented by Hoffman and Coutelle [15] in 1909. Harries [14] examined the product obtained by the heat polymerization of isoprene and in 1910 reported it to be similar in chemical and physical properties to natural rubber. In the same year, Lebedev [22] published the results of an investigation on the heat polymerization of conjugated dienes in which he stated that both butadiene and dimethylbutadiene gave rubber-like products in addition to various oily dimers. Subsequently he measured the amount of polymerization produced by heating various diolefines at 150° C.

Heat polymerization of the pure dienes is attended by serious limitations, as was shown by Lebedev, and more fully by Whitby and Crozier.[43] The chief limitations are that at elevated temperatures: (1) the diolefines form oily, dimeric by-products as well as rubber, and the proportion of the former is the greater the higher the temperature, i.e. the more rapid the polymerization ; (2) the degree of polymerization

TABLE 67. HEAT POLYMERIZATION OF ISOPRENE AND DIMETHYLBUTADIENE [43]

TIME Hours	ISOPRENE Oil %	Rubber %	Mol. wt	Relative viscosity [a]	DIMETHYLBUTADIENE Oil %	Rubber %	Mol. wt.	Relative viscosity [a]
				At 85° *C.*				
97·5	9·07	17·05	4589	4·62	—	—	—	—
101	7·9	16·25	—	—	0·9	10·5	2318	3·69
154	—	—	—	—	1·5	13·8	3345	3·83
250	—	—	—	—	2·7	19·6	3524	4·55
900	—	35·3	5715	8·20	—	49·7	3483	9·21
				At 145° *C.*				
5·25	38·2	10·03	3291	3·14	—	—	—	—
12·5	54·7	15·56	3936	4·69	11·1	15·6	2138	2·3

[a] Relative viscosity at 30·1° C. of a sol containing approximately 0·68 gram per 20 c c. of benzene.

of the rubber is not high, and the molecular weight of the product is lower the higher the temperature applied. It is generally accepted that superior products are obtained when polymerization is carried out at low temperature.

Isoprene at elevated temperatures has a much greater tendency than dimethylbutadiene to form oily, dimeric by-products instead of rubber. At 145° C. the oil formed is more than three times the amount of rubber. In great measure these conclusions hold generally for the polymerization of the other diolefines.

Catalysts. The use of catalysts is general in almost every form of production of rubber-like materials. The catalyst is of great importance. The factors concerned are :—

(*a*) Composition of catalyst.
(*b*) Preparation of catalyst.
(*c*) Shape of catalyst and particle size.
(*d*) Quantity employed.
(*e*) Activation of catalyst.

In each instance a catalyst of polymerization is usually present. This is generally an oxidizing agent, such as benzoyl peroxide, hydrogen peroxide, persulphates and so forth. A specific catalyst is sodium. In the case of olefines, the best catalysts are halides of boron, aluminium, titanium, etc. The process of polymerization is promoted by heat,

light, irradiation, or occurs spontaneously, and in some instances is further aided by pressure, notably when carried out in the gas phase.

There has been a tremendous amount of intensive work carried out to find more effective catalysts. The most widely used in commercial practice are the alkali persulphates. The most effective to date is

FIG. 32.—The Goodyear Synthetic Rubber Manufacturing Plant at Los Angeles.
View of a line of reactors

probably cumene hydroperoxide developed by the Hercules Powder Co. This cuts production time to about one-sixteenth the present time. It also enables effective polymerization at the low temperature of 40° F.

The following summary of a Russian alcohol process illustrates the significance they attach to the catalysts :—

1. The two components (1) and (2) of the catalyst must be intimately mixed in the ratio of 25 per cent. of (2) and 75 per cent. of (1). The

compound catalyst must be present in a form exposing the maximum possible active surface.

2. The alcohol must be evaporated and fully preheated to 450° C. before entering the catalytic chamber. In a plant operating at a capacity of 10,000 tons of SK rubber per year, this is accomplished by a single tubular evaporator and superheater. The evaporator is capable of handling approximately 11,000 kg. of alcohol per hour, and consumes 1,610,000 calories per hour, i.e. 328 calories per kilogram of alcohol.

3. Alcohol of 85 per cent. absolute concentration is used, mostly admixed with partly returning (unused) alcohol of 96 per cent. absolute concentration.

4. No substantial advantages can be derived from a change in the temperature of operation outside of the limits of 435°–450° C. The time of contact with the catalyst must be maintained at about 10 seconds.

5. For a factory of standard size (10,000 tons per annum), the equipment consists of 12 furnaces, mostly oil-fired, each containing 16 catalytic chambers, arranged in circular fashion. Each chamber is loaded with 90 kg. of catalyst. Each furnace received approximately 1,100 kg. of alcohol vapours per hour, and is capable of decomposing up to 750 kg. of alcohol vapours in this time, consuming 165,000 calories and producing 170–180 kg. of butadiene per hour. (These are figures based on a maximum yield of 25 per cent., which has been substantially improved.)

6. The catalytic reaction is continued for 11 to 12 hours, when the catalyst must be reclaimed, which is done by blowing it out with a mixture of air and steam at 500°–550° C.

7. The contact gases are cooled to approximately 150° C. by the incoming fresh alcohol, and then to about 80° C. with water.

Difficulty of Control. Diolefines are extremely reactive materials. They tend to polymerize with some ease, in some instances spontaneously. But with different conditions, the progress of polymerization very easily takes wrong turnings. Instead of straight-chain polymerization there may be cyclization and/or cross-linking, with formation of two- or three-dimension polymers. Too often the process may get out of hand. The lack of control inevitably results in poor products. It is consequently essential to establish a satisfactory routine which must be adhered to. It is no use obtaining at each cycle a rubber having very different properties.

According to Koch [19] it is certain that when butadiene is polymerized not only does the normal 1.4 addition occur to form long chains, but also 1.3 and 3.4 additions take place. Through this abnormal process

cyclization results. These molecular structural differences between natural rubber and Buna rubber may account for the poor processing properties of the latter, but may also explain such advantages as superior heat resistance and better abrasion resistance. There seems little doubt that long chain polymers without side branches are important for all products which must have high elasticity and elongation.

Sebrell and Dinsmore [33] have carried out extensive work on the structure of synthetic rubber-like materials, particularly in relation to their X-ray diagrams. They failed to get any characteristic pattern comparable with that obtained from natural rubber, in the case of Buna S, Perbunan, Thiokol, Chemigum and Vistanex. They considered therefore that the structure of these synthetic elastics is quite different from that of rubber and that they may owe their elastic properties to the operation of some completely different mechanism. They considered that there was probably considerable cross-linking of the chains.

Polymerization of diolefines to elastomers is complicated and not easily controlled. According to Williams [45] trouble begins as soon as the first molecule of diene is activated and polymerizes with a second molecule. This polymerization of two molecules with rearrangement of valency bonds leaves a new activated molecule, and a chain of reaction starts, which proceeds until terminated in some way. The reaction may terminate immediately, with production of cyclic products or it can proceed to build up into high molecular weight products. The final products may be rubbery materials of varying quality or balata-like thermoplastics. Plastic bodies may be formed which will change spontaneously into elastic products of a vulcanized nature.

In spite of great advances during recent years control of polymerization is still imperfect.

Diolefines do not polymerize in a regular manner. Branching and cross-linking are frequent. Until these are under control really satisfactory products will not be obtained. Even natural rubber does not consist of perfectly straight chains of isoprene. Standinger and Fischer have shown that branching does occur in the isoprene chains. This branching is however quite regular, in contrast to the chaotic branching in the synthetics. In fact, the regularity of the natural production lends credence to the idea that natural rubber may not be formed by a polymerization process.

The regular head-to-tail combination in the case of isoprene is thought to account for its crystalline behaviour. Many of the properties of synthetic rubbers, notably GR-S, are attributable to the erratic manner in which the molecules link up, some head to tail, some head

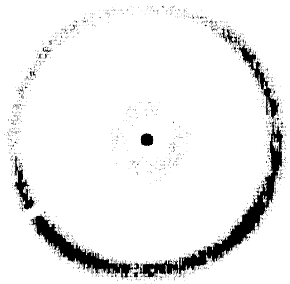


FIG 33 —X-ray Photograph of Unstretched Rubber.

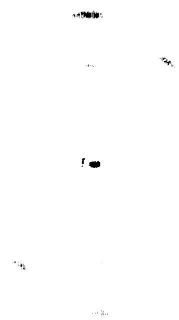


FIG. 34.—X-ray Photograph of Stretched Rubber (Sebrell and Dinsmore).

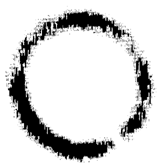


Fig. 35.—X-ray Photograph of Vistanex (Polyisobutylene) Unstretched (Sebrell and Dinsmore)

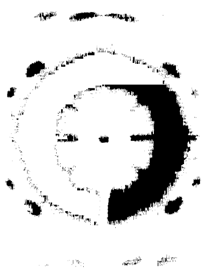


Fig. 36.—X-ray Photograph of Vistanex Stretched (Sebrell and Dinsmore).

to head, some tail to tail, and so on, added to the tendency for branching and cyclizing. These irregularities account for the non-crystalline behaviour of such materials. The possibilities of forming different combinations are endless. It also applies a degree of variability in the commercial materials which is of course the case. In order to keep the chains straight and to stop any tendency to cyclization, a chain straightener is added to the system. Probably the most successful up to the present have been the mercaptans used in the United States and the diproxid used in Germany.

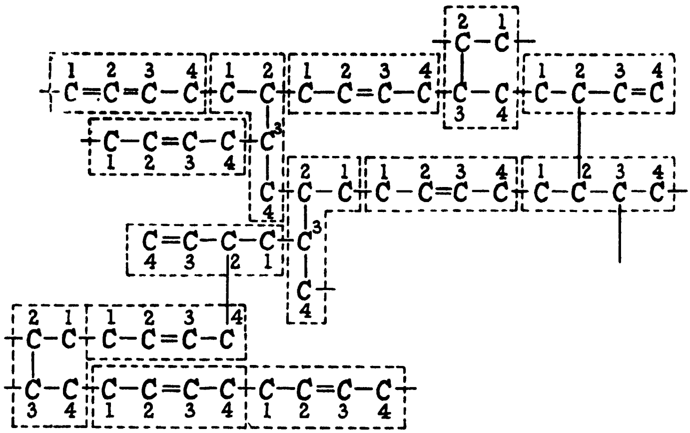


FIG. 37.—Butadiene Polymer according to Staudinger.

The crystalline structure in rubber is evident when it becomes stiff on stretching, whereas GR-S, for example, merely yields indefinitely These features emphasize the difficulties of control.

Williams [46] stressed the importance of the presence of foreign matter in the case of butadiene, which profoundly affected the direction of polymerization. The latest methods for production of butadiene reduce the significance of this factor.

Summarizing the earlier work, it was observed that diolefines were polymerized chiefly by heat processes, in the presence of one of an ever-growing number of catalysts. But the time factor was considerable and the quality of the rubber poor. Other methods were mere curiosities. The laboured procedure used by the Germans in the last war perfectly illustrated the disadvantages of all these methods.

Two major forms of procedure have gradually evolved. Until comparatively recently (about 1936) the methods based on the use of sodium as catalyst predominated. Inaugurated by Matthew and

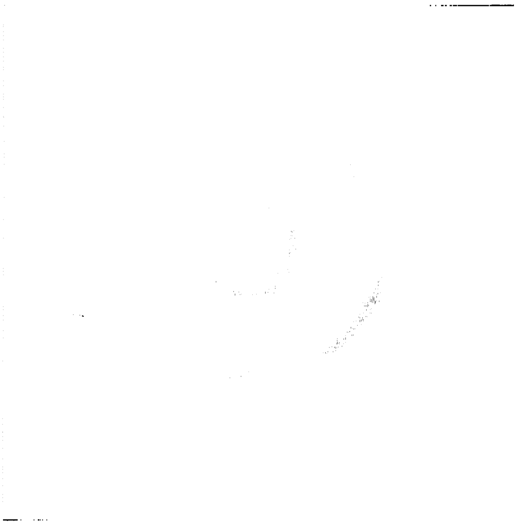


Fig. 38.—X-ray Photograph of Neoprene
(Sebrell and Dinsmore).

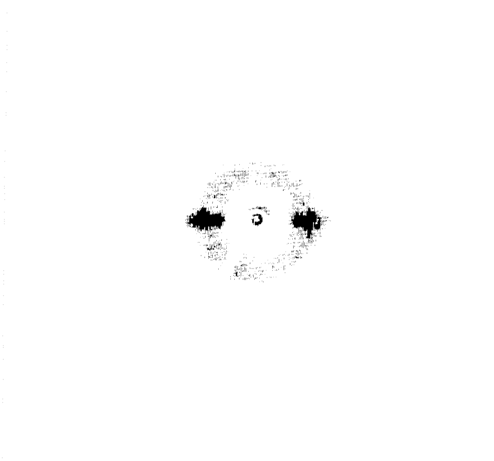


Fig. 39.—X-ray Photograph of Stretched Neoprene
(Sebrell and Dinsmore).

Strange,[27] *and by Harries, the sodium polymerization process passed* through all the various stages of development, and has been the basis of large-scale production, notably in U.S.S.R. and Germany. The I.G. has an almost interminable string of patents dealing with different aspects of the subject. It is to be noted that the German generic term "buna" is derived from *bu*tadiene and *na*trium.

Sodium Polymerization. The use of sodium (or potassium) as catalyst at first gave most unsatisfactory results. The products were extremely tough, and could not be brought to a reasonably plastic stage. They were also very difficult to vulcanize. For one thing sodium tends to react with butadiene. Polymerization proceeds irregularly and is difficult to control.

According to Abkin and Medvedev,[1] polymerization occurs heterogeneously with butadiene in the liquid phase; both in liquid and gas phases the rate of polymerization increases to a definite value and then remains constant. The first stage marks the formation of primary sodium butadiene compounds and lasts as long as metallic sodium remains in the system. Oxygen has a strong inhibiting effect on the reaction.

In the early days sodium was almost invariably used as wire. Many of the most recent processes have depended for their success upon variations of the form in which sodium is present. For example, it has been utilized as powder or as very fine spherical particles. Thus Tschajanov [40] described how butadiene was polymerized in a steel bottle using as catalyst a sodium dispersion in paraffin. A 99 per cent. yield was obtained after 63 hours. Zelmanov and Shalnikov [48] utilized colloidal sodium and obtained a rubber from butadiene in less than 36 hours at 10–15° C. using less than 0·3 per cent. sodium. Many of the most successful methods have used it in the form of surface films on formers of every conceivable shape.

The most powerful controlling factor in the sodium polymerization process has been the use of inert solvents. Stable, non-reactive, low-boiling hydrocarbons such as cyclohexane, petroleum ether, benzene, etc., were used in proportions of 10–20 per cent. Being swelling agents for the rubber which was produced they reduced the viscosity and increased the plasticity, moreover they facilitated the production of reasonable products from relatively impure dienes.

Bock and Tschunkur [3] polymerized isoprene with sodium in the presence of materials such as starch or ethyl cellulose in an inert atmosphere. For example, 100 parts of isoprene, 2 parts of sodium pieces, 1 part ethyl cellulose were introduced in hydrogen in an autoclave at 40° C. for 12 hours, yielding a soft elastic rubber.

Numerous other materials have been claimed to regulate the polymerization, including many vinyl derivatives. For example, 100 parts of butadiene with 0·3 per cent. of sodium and 1 per cent. of vinyl chloride at 60° C. was converted into polymerized butadiene in 30 hours.[16]

Cyclic diethers are also very effective.[17] Thus butadiene with 0·4 per cent. of sodium and 5 per cent. dioxane heated in an autoclave at 40° C. gave a solid product after 36 hours which could be vulcanized.

Ammonia and amines [18] have a similar effect, slowing the rate of reaction and keeping the temperature down, thus 0·5 per cent. of sodium and 0·05 to 0·10 per cent. aniline at 80° C. quantitatively polymerized butadiene in 30 hours.

Zavalkov [47] has described the method used at the Yaroslav plant in the U.S.S.R. to make S.K.B. rubber. Impure butadiene was used containing not less than 75 per cent. butadiene.

The batch was 1,700 litres, the reaction vessel being lined with paste of clay and glycerine. The sodium was present as a coating on 72 iron combs. The charge was heated at 30° C., the temperature being raised by 0·5° to 0·8° C. per hour for 8 hours. Cooling was necessary, the polymerization being exothermic, giving 349 cals. per kilogram of rubber formed. The maximum temperature was 65° C. at 8 atmosphere pressure, the reaction being finished after 120 hours.

According to Nebidovsky [29] butadiene is polymerized in nitrogen in an autoclave containing 5 per cent. of sodium deposited on zinc rods. After two hours the temperatureis raised to 30° C. and 8 atmospheres pressure. Polymerization is complete in 36 hours and 90 per cent. yield is claimed. The resulting rubber is said to be more resistant to friction, sunlight, oxygen, solvents and alkalies, than the natural rubber.

According to Ebert and Orth,[11] butadiene is continuously polymerized in the presence of an alkali metal as the polymerization catalyst, by introducing the material to be polymerized and the catalyst into a tube provided with a conveyor worm. The material is polymerized while thoroughly mixing it with the catalyst during forward movement through the conveyor. The finished product is withdrawn at the end of the tube.

The use of sodium as the major polymerizing agent now appears to be practised only in the U.S.S.R.

Until 1935, polymerization was carried out exclusively in jacketed, totally enclosed vessels, under pressure and at an average temperature of 50° C., using immersed, sodium-covered, paraffin-wax protected steel rods (so-called combs). In view of the exothermic nature of the

reaction (325 calories per gram of butadiene), the speed of reaction and the heat exchange have to be closely controlled. This makes the polymerization a lengthy process.

Since 1935, an alternative (the so-called rodless) method has been added and introduced on a large scale. In this process, polymerization takes place in a gaseous instead of liquid state (as far as can be judged from the scanty disclosures on the subject). The polymer produced in the gaseous state is less plastic, and is considered to be of superior quality and of greater uniformity than that formed in the liquid state.

The product is freed of the 2-butene which it contains after polymerization by a process of vacuum-kneading, simultaneously 0·5–1 per cent. of antioxidant, such as aldol-*a*-naphthylamine, is added.

The final step is refining. This is virtually a necessity because polymerization does not proceed entirely uniformly, and gives rise to overpolymerized strands, which have to be broken up and dispersed or removed. Ordinarily no attempt is made to wash out the sodium.

According to Koch the I.G. made Buna 85 by the sodium method, this being used mainly for hard rubber. In 1937 Konrad [20] referred to the effective use of sodium as catalyst for making Buna 85 and Buna 115. The trend is strongly in the direction of polymerization in aqueous emulsion, utilizing less stringent catalytic agents. This is a trend which applies equally well to the plastics industry.

Polymerization of Olefines. The first notable success of petroleum chemists in the synthetic rubber field was with polyisobutylene. There are a number of polyisobutylenes based upon isobutylene. As already described isobutylene is one of the chief olefines obtained by cracking processes. This is the material used in the United States. In Germany isobutylene is obtained by passing gaseous hydrocarbons through the electric arc.

Isobutylene may be polymerized by heating in the presence of catalysts such as aluminium chloride, boron chloride, stannic chloride, etc. Although it was found in 1873 by Butlerov and Gorianov [4] that isobutylene could be polymerized to a liquid product by means of sulphuric acid and/or boron fluoride as catalyst, it is only recently that rubbery products have been obtained. Standard Oil Development Co. and I.G. Farbenindustrie [34] purified light cracked oil to give a mixture containing at least 95 per cent. isobutylene. Crude oil containing butanes and butylenes was then added to produce a mixture containing from 20 to 40 per cent. of isobutylene, and 10 to 20 per cent. of other olefines. The mixture was then polymerized with boron fluoride at a temperature below 40° C., to yield plastic solid, or semi-solid rubbery materials. In another patent Standard Oil Development Co.[35] produced

high molecular weight polymers of olefines, notably polyisobutylene, *by passing the olefine into a bath of hydrocarbon diluent, such as ethane, propane, or butane, having an active catalyst, such as boron fluoride,* keeping the temperature below −10° C. Isoprene, styrene, and butadiene could also be polymerized by this method. Polymerization occurs with the formation of substantially straight-line polymers. The nature of these varies with the molecular weight, ranging from oily viscous fluids up to strong rubbery materials with molecular weights as high as 500,000.

FIG. 40—Reactors at the Goodyear Synthetic Rubber Manufacturing Plant at Los Angeles

The Use of High Pressure. There has been a certain amount of interest in the influence of very high pressures on the polymerization of diolefines, for polymerization of conjugated diolefines occurs with a great decrease in volume, which would therefore be aided by pressure. Conant and Tongberg [9] used pressures up to 1,800 atmospheres for the polymerization of isoprene. They found 10 per cent. was polymerized in 20 minutes at 23° C., while after 3 hours 76 per cent. was polymerized. The results obtained varied considerably in successive batches. According to Williams, the high-pressure polymer resembled vulcanized rubber in being both insoluble and non-plastic. He con-

sidered that the commercial application of pressure to polymerization *would present many difficulties.*

Starkweather [36] found that chloroprene polymerized eight times as fast at 6,000 atmospheres as at 3,000 atmospheres pressure.

There has been an enormous amount of work on high-pressure polymerization of ethylene. The main objective was to convert it into suitable fuels. But at least one outstanding commercial material with rubbery properties has emerged. This is the solid polymerized ethylene developed by Imperial Chemical Industries, Ltd., and known as polythene or alkathene.[12] It is prepared by heating ethylene at 100°–300° C. under a pressure of at least 1,200 atmospheres, when solid or semi-solid polymers are formed.

Although most polymerizing processes on isobutylene have been carried out at very low temperature, yet according to Kuentzel and Webb [21] interesting resinous products are obtained by submitting it to pressures of 300 atmospheres at temperatures as high as 100° C.

Polymerization by Light. The effect of photochemical action on monomers is best brought out by its use in the case of polyvinyl chloride.

Regnault,[32] Bauman,[2] and Ostromislensky [30] used sunlight and ultra-violet rays to polymerize vinyl chloride.

According to Ostromislensky, the polymerization was effected by irradiation from a mercury quartz lamp for 12 hours at 20° C.

Ostromislensky classified the resultant polymers as alpha-, beta-, gamma- and delta-, polyvinyl chlorides, according to solubility in acetone or chlorbenzol; α-polymer is soluble in acetone; β-polymer is soluble in chlorbenzol; γ- and δ- polymers are insoluble in chlorbenzol.

In the opinion of Ostromislensky, in the photopolymerization the process progresses with formation at first of α-polymer, which, under the continued action of ultra-violet rays, is converted into the β- form; the transformation of vinyl chloride into γ- and δ-polymers is conditioned by a further prolonged action of the ultra-violet radiation.

In order to ensure a high degree of dispersion of polyvinyl chloride molecules the photochemical process, like the thermo-polymerization, may be conducted either in a solvent (e.g. alcohol, acetone, dichlorethane, etc.) or in emulsions.[10]

The problem of the photopolymerization of vinyl chloride in various solvents has been investigated by Plotnikoff,[31] and the colloidal properties of vinyl chloride polymers derived in different solutions were examined by Flumiani.[13]

The results of these researches showed that the speed of poly-

merization of vinyl chloride in solution, at constant concentration, depends on the nature of a solvent; for example, the comparative values of polymerization velocities in toluene is 1, in ethyl alcohol 25, and in carbon tetrachloride 68.

The effect of the ultra-violet rays upon the liquid vinyl chloride is so intense that the formation of polymers occurs almost spontaneously. It would seem, therefore, that out of numerous methods the photo-polymerization of vinyl chloride has the most favourable chances of application, since it allows a continuous rapid procedure. There are certain difficulties of control which impede progress.

The Mechanism of Polymerization. Melville[28] has summarized the information available about the mechanism of the combination of substances of high molecular weight. Considerable progress has been made in this branch of chemical kinetics. In general, high polymers are formed by polycondensation reactions or by the union of ethylene derivatives into chain-like molecules. The latter is the interesting type for consideration in the study of synthetic rubbers. In the case of ethylene derivatives considerable progress has been made because the reaction can be followed in the liquid and in the gaseous phase. According to Melville these reactions are substantially chain reactions. He stated that the derivatives most susceptible to polymerization are the vinyl compounds of the general type $CH_2{:}CXY$; the substituent groups have a great influence on the course of the reaction. In general the more highly polar X or Y is, the more readily is the polymer formed. The evidence that the reactions are of the chain type depends on the fact that small amounts of catalyst or of radiation will produce large amounts of the polymer. Yet these reactions are easily stopped by anti-oxidants. According to Melville the chain carrier is the growing polymer which is in a very reactive state. So that when it collides with a monomer molecule the latter adds on quite easily involving a small amount of activating energy. When reactions are induced by addition of free radicals it seems clear that the growing polymer is simply a large free radical with a terminal free valency. It is, however, difficult to explain by this mechanism alone such reactions as photo-polymerization of chloroprene and of methyl methacrylate. Melville pointed out the striking property that these materials continue to polymerize in the dark, showing that the molecules exist for a long period. Another interesting feature is that these active molecules enable the development of heterogeneous polymers, so that it is possible to grow chloroprene on an active centre of polymethyl methacrylate. Since the action is subject to specific chemical inhibition it is probably chemical in nature. Melville stated that the structure of vinyl polymers

has been established in several ways. By analogy with the behaviour of quite small molecules it seems that the predominating structure is of the head to tail type. X-ray evidence too, in general, supports this opinion. Also the way atoms or groups may be removed, for example, chlorine from polyvinyl chloride, also tends to confirm this.

It is now fairly generally accepted that vinyl polymerization induced by catalysts proceeds by the formation of free radicles. The essential steps are initiation—propagation—termination. In diene synthesis, the procedure differs inasmuch as the initiation may consist in either 1,4- or 1,2- addition to the diene system or both may occur in random fashion with a consequent tendency towards cyclization.

REFERENCES

[1] ABKIN and MEDVEDEV, *Trans. Faraday Soc.*, 1936, **32**, 286.
[2] BAUMANN, *Ann.*, 1872, **163**, 308.
[3] BOCK and TSCHUNKER, B.P. 283,840/1927.
[4] BUTLEROV and GORIANOV, *Ann.*, 1873, **169**, 146.
[5] CAROTHERS, *Ind. Eng. Chem.*, 1934, **26**, 30.
[6] CAROTHERS, BERCHET and COLLINS, *J. Amer. Chem. Soc.*, 1932, **54**, 4071.
[7] CAROTHERS and COFFMAN, *J. Amer. Chem. Soc.*, 1932, **54**, 4071.
[8] CAROTHERS, KIRBY and COLLINS, *J. Amer. Chem. Soc.*, 1933, **55**, 789.
[9] CONANT and TONGBERG, *J. Amer. Chem. Soc.*, 1930, **52**, 1659.
[10] DOUGLAS, *Ind. Eng. Chem.*, 1940, **32**, 315.
[11] EBERT and ORTH, U.S.P. 2,209,746/194.
[12] FAWCETT, GIBSON, PATON, PERRIN and WILLIAMS, B.P. 471,590/1936.
[13] FLUMIANI, *Koll. Zeit.*, 1928, **45**, 152.
[14] HARRIES, *Ann.*, 1911, **228**, 383.
[15] HOFFMAN and COUTELLE, G.P. 250,690/1909.
[16] I.G., B.P. 324,004/1929.
[17] —— B.P. 283,840/1927.
[18] —— B.P. 347,802/1932.
[19] KOCH, *Ind. Eng. Chem.*, 1940, **32**, 464.
[20] KONRAD, *Kautschuk*, 1937, **13**, 2.
[21] KUENTZEL and WEBB, U.S.P. 2,221,000/1940.
[22] LEBEDEV, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949.
[23] —— *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1377.
[24] MARK, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Leipzig, 1930.
[25] MARK and RATH, *High Polymeric Reactions*, New York, 1941, p. 81.
[26] MARVEL, *J. Amer. Chem. Soc.*, 1930, **52**, 376 *et seq.*
[27] MATTHEWS and STRANGE, B.P. 24,790/1910.
[28] MELVILLE, *J. Inst. Chem.*, 1942, Part 6, p. 264.
[29] NEBIDOVSKY, *Bull. Ass. Chim.*, 1938, **55**, 215.
[30] OSTROMISLENSKY, G.P. 264,123/1912.
[31] PLOTNIKOFF, *Z. wiss. Phot.*, 1922, **21**, 117.
[32] REGNAULT, *Ann. Chem. Phys.*, 1838, **65**, 157.
[33] SEBRELL and DINSMORE, *I.R.W.*, 1941, **103**, 37.

[34] Standard Oil Development Co. and I.G., B.P. 407,932/1937.
[35] Standard Oil Development Co., B.P. 481,646/1937.
[36] STARKWEATHER, *J. Amer. Chem. Soc.*, 1934, **56**, 1870.
[37] STAUDINGER, *Die hochmolekularen organischen Verbindungen*, Berlin, 1932.
[38] STAUDINGER and FROST, *Ber.*, 1935, **68**, 2351.
[39] THOMPSON, *Polymerization*, New York, 1937, p. 16.
[40] TSCHAJANOV, *Sintet. Kautschuk*, 1935, **4**, 28.
[41] WHITBY, *Trans. I.R.I.*, 1930, **5**, 184.
[42] —— *Faraday Society Symposium on Polymerization*, 1935, 312.
[43] WHITBY and CROZIER, *J. Can. Research*, 1932, **6**, 203.
[44] WHITBY and GALLAY, *J. Can. Research*, 1932, **6**, 280.
[45] WILLIAMS, *Polymerization*, New York, 1937, p. 169.
[46] —— *ibid.*, p. 170.
[47] ZAVALKOV, *Kautschuk*, 1934, **2**, 15.
[48] ZELMANOV and SHALNIKOV, *J. Phys. Chem. Soc. U.S.S.R.*, 1933, **4**, 453.

CHAPTER 9

COPOLYMERIZATION

In spite of all the advances made in the polymerization of the butadienes, etc., it became increasingly apparent that the materials obtained, although good in themselves, were not good enough. While sharing many of the good properties of rubber, they also had the disadvantages. It was also evident that while no single monomer had all the desirable characteristics, yet considered together with available vinyl monomers, it became clear that the properties of any one were often complementary to those of another. The introduction of copolymerization provided a solution to this problem of bringing suitable polymers together.

In this manner many synthetic elastic materials have been obtained, having some property, or properties, far superior to natural rubber. An enormous amount of work has been carried out along these lines. Although at first it was thought that admixture of different diolefines would give beneficial results, this has been abandoned in favour of the copolymerization of a diolefine with a synthetic resin. All the variations of this theme are now being worked out. Each new synthetic resin is tried out as it appears.

Copolymerization. In recent years the new technique of copolymerization has been evolved which not only goes far towards solving the problem, but has opened up further new fields for materials capable of polymerization. For example, a fairly good synthetic rubber can be made by polymerizing isoprene or butadiene alone, either in a single-phase system or in an aqueous emulsion. Better products can be made by copolymerizing these hydrocarbons with other compounds containing active vinyl groups such as styrene (vinylbenzene) acrylonitrile (vinylcyanide), vinylidene chloride, methyl vinyl ketone, methyl methacrylate, or any of a hundred other vinyl-substituted hydrocarbons, chlorinated hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, esters, nitriles, etc. Another interesting group of synthetic rubbers comprises the copolymers of a diene, such as butadiene, with an olefine, such as isobutylene. Then, too, there are the polymers of chloroprene and, like butadiene, chloroprene can be interpolymerized with a wide range of vinyl compounds to give commercially valuable products. Moreover, diolefines may be polymerized with other diolefines, e.g. butadiene with chloroprene—and

there are many three-way copolymers which possess unique and interesting properties. There is almost no limit to the range of synthetic elastics which can be made. Instead of mixing the polymers, the original monomeric substances are brought together and are then polymerized to the desired degree.

This is the process known as copolymerization, interpolymerization, or mixed polymerization. Copolymerization is probably the best term, and should be recognized as a standard description. The process may

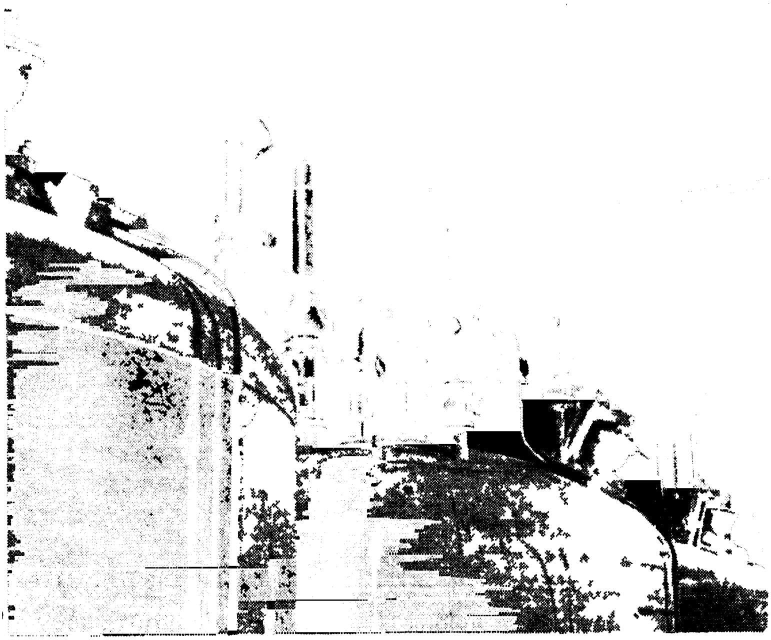


FIG 41 —Glass-lined Reactors used for Polymerization

be carried out upon mixtures of the monomers as they are, in solution or as emulsions. The method adopted has, however, a profound influence on the properties of the product.

At first sight it would appear that a mixture of the two separate polymer types would be formed. Actually this is not the case. Entirely new materials result, in which both monomeric groupings are found in the same polymerized molecule.

The properties of the materials are different from what might be anticipated. They are not intermediate between the two types. Generally they are much improved, while there are certain new characteristics that are of great value. Whereas with mechanically mixed

polymers the individual ingredients may be separated, for example, by the use of solvents, yet in the case of copolymers such a separation is not possible. The solubility of a copolymer may be very different from those of the components. For example, while vinyl acetate and vinyl chloracetate each polymerize to give soluble products, the copolymer is virtually insoluble in the same solvents.

The Outstanding Copolymer. Consideration of the products obtained from vinyl chloride and vinyl acetate admirably illustrates the effects of copolymerization.

Vinyl acetate polymerizes to give polyvinyl acetate. This is quite useful commercially, and is widely employed as an adhesive; it is brittle although it softens between 30° C. and 40° C. It is exceptionally resistant to heat and light. Owing to the low softening temperature it cannot be processed and moulded with any ease. It also has a relatively high water absorption. A typical ester, it is fairly active chemically; for example, undergoing saponification in the presence of alkalis. It is soluble in alcohols, ketones, esters, chlorinated hydrocarbons and aromatic hydrocarbons.

Polyvinyl chloride is quite different. It has a very high softening point and is not very thermoplastic. It is chemically inert, virtually non-inflammable, tasteless and odourless. It has great resistance to corrosion, not being attacked even by acids such as sulphuric, nitric and hydrochloric, nor is it affected by alkalis. It has extremely low water absorption.

Furthermore it is almost insoluble in all solvents in the cold, although it dissolves fairly readily in hot chlorinated hydrocarbons such as ethylene dichloride. It is not particularly stable to light and heat. This material is unusually strong and water and chemical-resistant, but it softens so slowly with rise in temperature that decomposition begins before it can be properly moulded. For this reason the resin is always plasticized by mixing on a hot roll mill or in a jacketed dough mixer with a plasticizer, usually a compatible high-boiling liquid such as tricresyl phosphate. Upon cooling, a resilient rubber-like mass is formed which has been used successfully in numerous applications requiring greater resistance to sunlight, oxidation, oils, and greases than is exhibited by rubber. Such uses include wire insulation, tubing, impregnated cloth for raincoats and shower curtains, and linings for acid-resistant containers. The poor solubility of polyvinyl chloride in most organic solvents limits its use in the surface coatings field.

Consideration of the properties of these two vinyl compounds showed that if they could be combined a useful material should be obtained. Mechanical admixture of polyvinyl acetate and polyvinyl

chloride was tried from every conceivable angle, but they were incompatible and the resulting mixtures were invariably too weak and brittle. It was then found that when the monomeric vinyl compounds were polymerized together, a resin was formed that retained the strength and water resistance of polyvinyl chloride but that had been sufficiently plasticized internally by the combined polyvinyl acetate to make it mouldable at temperatures within the range of its heat stability and soluble in many organic solvents. Thus a resin molecule was formed that consisted of a linear chain in which monomeric vinyl chloride and vinyl acetate had reacted with themselves and with one another at the double bond to form a copolymer. The relative proportions of vinyl chloride and vinyl acetate in the chain depend upon the composition of the reaction mixture; and the length of the molecule, as in the case of other vinyl polymerizations, is governed by reaction conditions at the instant of formation. Average molecular weight may also be controlled by fractionation and extraction. Extraction is accomplished by partial precipitation or by treating the finely divided dry resin with an appropriate solvent-nonsolvent mixture that dissolves out the lower polymers and leaves the higher bands intact as a granular powder.

The copolymerization of these compounds makes possible the synthesis of a wide range of resins suitable for a variety of industrial applications. Not only is it possible to vary the average molecular weight as in the case of other vinyl resins to suit the application involved but to alter the vinyl chloride-vinyl acetate ratio as well.

Thus, in common with other vinyl resins, increase in the average molecular weight or degree of polymerization of these copolymers results in greater strength and toughness but makes the resin more difficult to mould or to put into solution. Electrical properties, specific gravity, refractive index, and water resistance remain constant. On the other hand, increase in vinyl chloride content improves water resistance and raises the softening temperature, but yields a less soluble and less easily moulded product.

The copolymers formed in this way are found to be thermoplastic, odourless, tasteless, and non-inflammable. The mechanical properties are considerably higher than could have been visualized. Not only is the tensile strength very high, but the products are extremely tough and have a measure of resilience. The electrical properties are very good. The resistance to moisture is extremely high. The resistance to corrosion and chemical attack is exceptionally good, while the products are unaffected by soaps, acids, alkalis, oils and alcohol.

The scope of the copolymer is extremely wide, for it is extremely

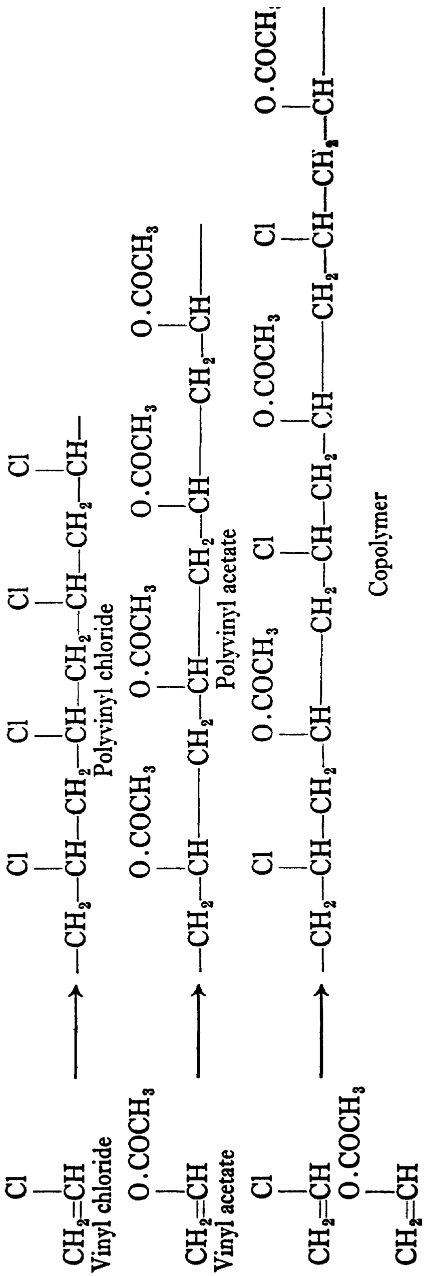


FIG. 42.—Copolymerization of Vinyl Chloride and Vinyl Acetate.

versatile and can be worked or moulded without difficulty on rubber or plastics machinery.

The properties of any particular copolymer depend upon the molecular weight or, in other words, the degree of polymerization, upon the ratio of the two polymers, and upon their distribution. The latter factor in turn depends upon the method of production.

The actual distribution of the respective components along the copolymer chain is a matter of some uncertainty. It can be controlled within reasonable limits only by maintaining rigid control of the conditions under which the polymerization is carried out. Any deviations may lead to the production of products having different properties. Since the molecular chains may contain some hundreds of the monomer

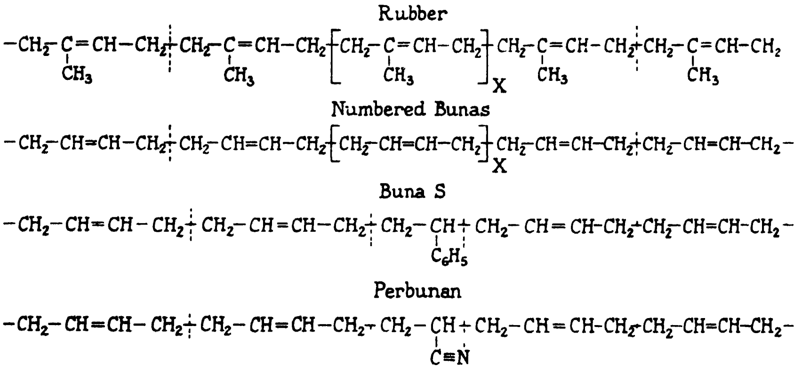


FIG. 43.—Chain Molecules of Rubber and some of the Buna Elastomers.

units joined together, there is evidently some scope for variation in the positions. It is these factors which make the reproduction of successive batches to have absolutely identical properties rather difficult.

In general, it has been found that the mechanical properties improve with a rise in the degree of polymerization, while the other properties are more or less independent of this, being rather a function of the chemical composition. In deciding upon a copolymer for any specific application, a type is naturally chosen that combines as many desirable properties as possible with a minimum of undesirable ones.

Copolymerization and Synthetic Elastics. There has been great activity in the production of synthetic rubbers and similar materials by copolymerization of butadiene and other compounds. It is now the principal method used.

Synthetic rubbers made by straightforward polymerization have been found to have very marked limitations. By forming copolymers,

each product possesses the general rubbery properties, but some additional specialized characteristic in addition. The formation of copolymers enables the production of materials which can be described as having "rubber-synthetic resin" characteristics, or "synthetic resin-rubber" characteristics according to whether the rubber component (butadiene, chloroprene, etc.) predominates, or the synthetic resin component (styrene, methyl methacrylate, etc.) predominates.

These are well illustrated by the different types of Buna rubber, the German elastomers. The early types were based on experience obtained during the last war, and were found to be unsatisfactory in many respects. The copolymerization process has facilitated the production of successful materials, having properties which are specially suited for definite applications.

The production of these copolymer synthetic rubbers proceeds apace; new types are being developed daily, although naturally many are found not to be suitable for commercial purposes.

Considering the various leading types of synthetic rubber-like materials the importance of copolymerization becomes quite unmistakable.

Perbunan is a copolymer of butadiene and acrylic nitrile; so are Hycar and Chemigum. Thiokol RD is also a copolymer. Buna-S is a copolymer of butadiene and styrene. Some of the newest types of neoprene are copolymers of chloroprene and other monomers. Butyl rubber is a copolymer of isobutylene and isoprene. And the same trend is equally marked in plastics production.

According to Mueller,[14] both copolymers S and N can be considerably changed in quality by changing the ratio of butadiene : styrene or butadiene : acrylonitrile, respectively resulting in softer or harder, tougher products. When one gram-mol of butadiene, 54 grams and one gram-mol of acrylonitrile, 53 grams, are used for the reaction, which is equal to a 1 : 1 ratio, a good grade of Buna-N is obtained. In the case of Buna-S the molecular ratio is approximately 1 : 2 as the molecular weight of butadiene is 54 and that of styrene 104.

A considerable volume of work confirms that the properties of copolymers can be modified profoundly by varying the proportions of the respective polymers. The Americans in particular have produced numerous copolymers of the GR-S class.

The following selection of some recent rubber-like copolymers shows how actively this angle is being studied. Moreover, work is being carried out employing more than two monomers.

The I.G. made copolymers of butadiene with 2-vinyl furane,[9] the products being capable of vulcanization. In another patent [11] it was

vinyl ethenyl carbinols which were copolymerized together with butadiene products to give synthetic rubbers. Other examples of copolymer synthetic rubbers include the following:

In one patent,[10] the I.G. polymerized butadiene and an ethylene dicarboxylic acid in aqueous emulsions using an oxidate catalyst. An example described the copolymerization of 75 parts fumaric acid ester and 25 parts butadiene. Konrad and Bock [13] polymerized an aqueous emulsion of a butadiene hydrocarbon with 40 per cent. of an acrylic, methacrylic, etc., derivative.

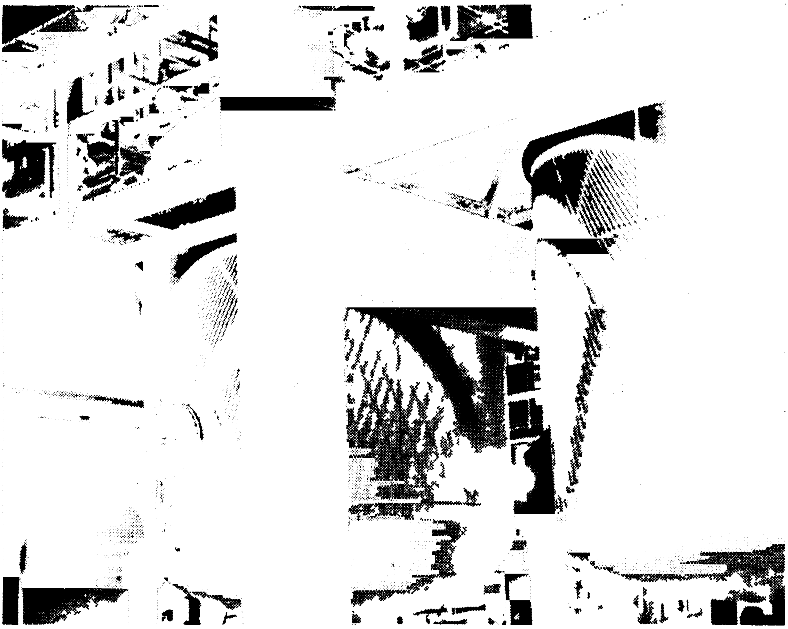


FIG 44—After the Molecules of Butadiene and Styrene have combined in the Reactors the Batch is drawn off into "Blow-down" Tanks Here, the Reaction is stopped The Butadiene and Styrene which did not enter into Reaction are then recovered

Muller-Conradi [15] and Daniel polymerized a butadiene emulsion in the presence of emulsions of highly polymerized isobutylene with the aid of peroxides. The products were claimed to be far superior to those obtained from butadiene alone.

Another rather good example is the following patent of the Wingfoot Corporation: [17]

Butadiene is co-polymerized with vinylidene chloride to give vulcanizable rubber-like polymers. The 1.3 butadiene is preferred, but its homologues may also be used. From 50 to 65 per cent. of the butadiene component

should be present to obtain products most nearly resembling rubber. Polymerization is best effected by heating aqueous emulsions containing sodium oleate or similar emulsifying agents, catalysts such as benzoyl peroxide or sodium perborate, and promoters such as carbon tetrachloride or trichloropropionitriles.

In this country too, there has been some activity along these lines. In one patent Habgood, Hill and Morgan [7] copolymerized butadiene with half its weight of specified methacrylic acid esters in the presence of 5 to 30 parts carbon tetrachloride. In another [7] they copolymerized a chloroester of methacrylic acid with butadiene, while in yet another patent they showed how to copolymerize methyl methacrylate with butadiene.

Extremely interesting copolymers have been made from butadiene and methacrylates by Du Pont de Nemours.[6] They prepared the following table to show the effects of different proportions of the ingredients.

TABLE 68

Butadiene %	Methyl methacrylate %	Properties
4	96	Soluble resin more flexible than polymerized methyl methacrylate
6	94	More flexible than preceding resin
8	92	Fairly tough soluble resin
10	90	Fairly tough soluble resin
12	88	Tough soluble resin
16	84	Somewhat softer more pliable resin
20	80	Insoluble rather soft pliable material
30	70	Insoluble soft rubber-like copolymer

Borders, Juve and Hess [4] described a typical copolymer in which styrene was the predominating polymer. This product consisted of 85 parts of styrene and 15 parts of butadiene. While not rubbery, it has proved an excellent compounding ingredient under the name of Pliolite S3.

The laboratories of the world are working overtime to produce the various copolymers, trying out the whole range of diolefines and vinyl compounds one after the other.

The Process in Specific. The process of copolymerization is specific. That is to say, that it does not follow that admixture of any two vinyl monomers or a diolefine and a vinyl monomer will inevitably produce a copolymer. For example, styrene and vinyl acetate will not polymerize together. All that happens is that the styrene polymerizes

in the normal way to yield polystyrene, while the vinyl acetate remains unchanged. The nature of the radical attached to the parent nucleus has a profound bearing on this ability to yield copolymers.

Another important point is that the presence of minute quantities of certain materials act as very effective poisons, inhibiting the reaction. One example is the case of the copolymerization of butadiene and acrylic nitrile, normally presenting no difficulty, which is completely stopped by the presence of minute traces of copper or certain amines.

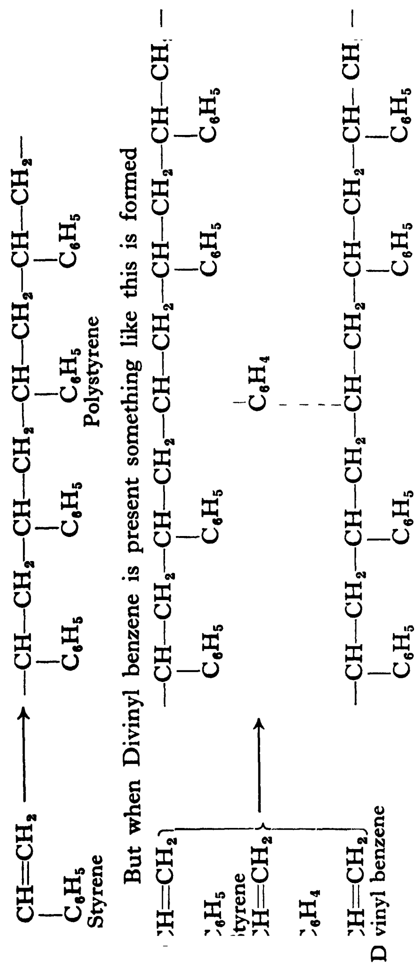


Fig. 45.

Addition of Small Amounts of Secondary Ingredients. Yet another important aspect of copolymerization has yet to be considered.

It has recently been shown that by utilizing small quantities of specially selected secondary materials that it is possible completely to modify characteristic properties of the polymers. Thus the introduction of small amounts of divinyl compounds to ordinary vinyl materials is found to give insoluble polymers by contrast to the polymerized vinyl compound which is soluble in the solvent in question. It is considered that these additions give the long-chain molecules a very pronounced three-dimensional character.

Staudinger and Heuer [16] showed that additions of small amounts of divinyl-benzene to styrene yielded, after polymerization, an insoluble polymer which would only swell to a limited extent in solvents in which polystyrene is freely soluble.

This was thought to operate because the divinyl benzene caused the normally unbroken straight chain of polystyrene to branch when one of these molecules joined in. Each branch would proceed from a certain length, would again pick up a divinyl-benzene molecule and would then branch again. In this way a three-dimensional structure is rapidly built up, a fact which is considered to modify profoundly the behaviour of materials in solvents. It only needs comparatively few molecules of the divinyl compound to exert a very marked effect.

It is interesting to note that GR-S 60, one of the more important new American products, is made by polymerizing butadiene and styrene together with a little divinylbenzene.

In the synthetic elastic field the outstanding example of this type of copolymerization is butyl rubber. In this instance, addition of a small amount of a diolefine butadiene is able completely to change the properties of the predominating ingredient—isobutylene. Less than 2 per cent. of butadiene or isoprene is present, yet the polymerized product can be vulcanized, in complete contrast to the polymerization of isobutylene which results in the thermoplastic polyisobutylene which cannot be vulcanized.

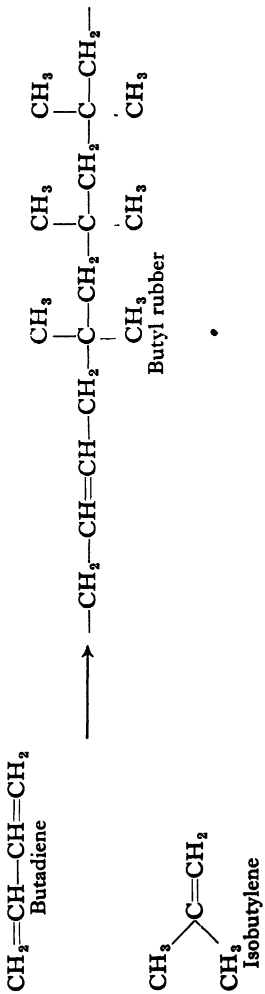


FIG. 46.—Butyl Rubber—A Copolymer.

How Monomers Link Up in the Copolymer Chain. A certain amount of work has been done on the elastomers to determine how the respective polymers link up, whether they alternate in a regular manner or whether there is haphazard linking. Alekseeva [1] investigated the structure of butadiene and acrylic nitrile made by polymerizing an equimolecular mixture in emulsion at 60° C. for 116 hours. She subjected a solution to ozone treatment and then hydrogen peroxide, along the lines laid down by Harries. The resulting mixture of acids was analysed. It was found

that one-half of the product was formed by an alternate succession of butadiene and acrylic nitrile in the molecule. About one-third consisted of molecules where one butadiene unit corresponded with two or three molecules of acrylic nitrile.

She [2] also examined the copolymer of butadiene and methacrylic acid nitrile by a similar technique, obtaining a mixture of acids which were separated as methyl esters. This yielded 62 per cent. by weight of 2-methyl- 1, 2, 4-butane tri-carboxylic acid and 8 per cent. succinic acid. It showed that the copolymer was mostly built up of alternate units of each monomer with 1,4 addition to the butadiene molecule.

Alekseeva and Belitsraya [3] applied to a Buna-S material the same process of ozonolysis, followed by hydrogen peroxide oxidation. This gave a mixture of formic, succinic, phenyladipic, and diphenylsuberic acids, as well as a high molecular weight acid of undetermined structure. From the amounts of these acids it was calculated that the polymer consisted of mixed products, in which 31·2 per cent. of the styrene was joined by 1-4 addition alternately to butadiene units, 40 per cent. of styrene was in a union in which two units of styrene were joined in 1-4 positions to one or several units of butadiene, and 29 per cent. of styrene was united to butadiene in the 1-2 and 1-4 positions. Of the butadiene 23·3 per cent. was polymerized through 1-2 positions and the rest through 1–4 positions.

The fact that the styrene units are not evenly spaced along the chain explains many of the troubles encountered in GR-S. GR-S shows no tendency for crystallization. This is clearly due to complete lack of symmetry in the polymer chains. Ozonolysis shows that the styrene groups are not evenly spaced but are sometimes even grouped together. In the strictest sense GR-S is not a true polymer.

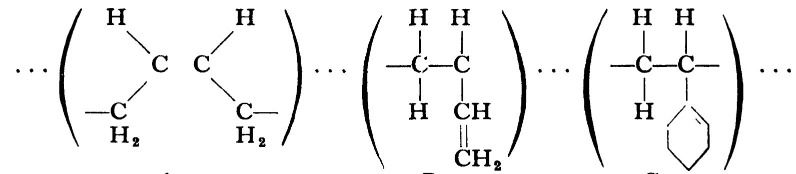
Kemp and Straitiff [12] have given a clear description of this idea.

The absence of crystallization in GR-S can be explained on the basis of non-symmetry along the polymer chains. Strictly speaking, GR-S is not a true polymer since ozonolysis shows that the styrene units are not evenly spaced in the chain but are grouped together in some locations. Ozonolysis also has proved the presence of vinyl groups attached to the chain, resulting from the polymerization of butadiene in the 1,2 instead of the 1,4 position. These vinyl groups must be unevenly spaced along the chain, and mixed trans and cis isomers must be present.

Fig. 47 illustrates the chemical units present in GR-S, rubber, and gutta-percha hydrocarbons. In a GR-S copolymer containing 24·5 per cent. styrene, there are six butadiene units to one styrene unit. It appears that about one butadiene in five polymerizes in the

1,2 position in the chain. It should be emphasized that in GR-S, ozonolysis has shown that no regular order exists in the location of A, B and C units in the polymer. An entire lack of symmetry in the positioning of these units in the chain would be expected in view of the nature of the polymerization reaction.

Consequently, we can readily see how impossible it is for GR-S to crystallize. Since double bonds in the butadiene chain units and in the vinyl groups are unevenly spaced along the chain, they cannot be uniformly or frequently matched up with those in neighbouring chains. This fact may result in an effectual cross-linking of GR-S chains with active sulphur atoms during vulcanization. In contrast, the more or less perfect chain symmetry of sol rubber hydrocarbon



A
1,4
cis or trans

B
1,2

C

FIG. 47.—Part of a GR-S chain.

should result in a higher frequency of alignment of the double bonds and, therefore, a more effective vulcanization reaction to produce more frequent and more evenly space cross-links in the vulcanizates.

Where vinyl and benzene side groups are located in the GR-S chain, the separation of adjacent chains will be considerably greater than in natural rubber chains with shorter methyl side groups. This wider chain separation of GR-S chains may also reduce effective cross-linking with sulphur during vulcanization and thereby cause weak areas in the vulcanizate structure.

It appears to be established that the isoprene component in butyl rubber is not regularly spaced in the copolymer chain.

Cheyney and Kelly [5] have investigated the degree of unsaturation of elastomers. They used the Wijs method on sodium butadiene polymer, and on copolymers of butadiene-styrene and butadiene-acrylic nitrile. Reaction was much slower than with rubber, taking 24 hours at 30° C. to complete the additional reaction. After this substitution occurs in the butadiene polymer and cyclization in the copolymers. They found the iodine values to show 4 per cent. cross linkage in the styrene copolymer and 10 per cent in the sodium polymer.

REFERENCES

[1] ALEKSEEVA, *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 1426.
[2] —— *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 353.
[3] ALEKSEEVA and BELITSRAYA, *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 358.
[4] BORDERS, JUVE and HESS, *Ind. Eng. Chem.*, 1946, **38**, 955.
[5] CHEYNEY and KELLY, *India Rubber World*, 1942, **106**, 585.
[6] Du Pont de Nemours, B.P. 544,341/1942.
[7] HABGOOD, HILL and MORGAN, B.P. 467,244/1936, 478,593/1937, 485,941/1937.
[8] HABGOOD and MORGAN, B.P. 511,838/1939.
[9] I.G., B.P. 487,604/1937.
[10] —— B.P. 497,841/1938.
[11] —— B.P. 50,703/1939.
[12] KEMP and STRAITIFF, *Ind. Eng. Chem.*, 1944, **36**, 707.
[13] KONRAD and BOCK, G.P. 667,163/1939.
[14] MUELLER, *India Rubber World*, 1942, **106**, 34.
[15] MÜLLER-CONRADI and DANIEL, *Kunststoffe*, 1939, **29**, 242.
[16] STAUDINGER and HEUER, *Ber.*, 1934, **67**, 1164.
[17] Wingfoot Corporation, B.P. 533,142/1931.

CHAPTER 10

EMULSION POLYMERIZATION

The Growing Use of Emulsions. The current trend with synthetic elastics, and indeed with most synthetic materials, is to polymerize in emulsion. The evident intention is to simulate the simple processing of nature. And the time factor has been much reduced, so that in 1933 Whitby and Katz [26] could comment " most of the newly patented processes are claimed to produce a synthetic rubber after only a few days of polymerization, as compared with the period of several months required by methods used in Germany during the war ". It is now possible to carry out the process in a few hours. More important still, the process has been brought on to a continuous basis and it is only a matter of time before the conversion will be completed in minutes and not hours. According to Dinsmore [7] polymerization in emulsion without catalysts takes six months at 50° C. Already *redox* catalysis can effect polymerization within an hour.

It is interesting to note how the production of synthetic rubber begins to approximate to the production of natural rubber, where nature, using air, carbon dioxide, and water, with the aid of solar energy produces presumably isoprene which is then converted catalytically and continuously into rubber in the form of an aqueous dispersion-rubber latex. Synthetic rubber production begins to follow the pattern. As in many other aspects of synthetic work this seems to be the right line. It is interesting to observe that this remarkable change in the perspective of those engaged in making synthetic materials corresponds with the real arrival of the synthetic materials on a commercial scale. As a direct consequence of this trend there are now available commercially latices from copolymers of butadiene and styrene; copolymers of butadiene and acrylonitrile; polymers of chloroprene; polymers of thioplasts; and a whole range of plastics.

Synthetic elastics have had very chequered careers. There have always been many disadvantages associated with them. These should be regarded as teething troubles, for from the commercial standpoint synthetic rubbers are still in their infancy. For many years it has been accepted that these materials must inevitably possess extremely unpleasant odours and poor colour. Other unsatisfactory features were associated with the difficulty of processing them. As events have shown

these disadvantages are not inherent, but are merely the results of unsatisfactory methods of production.

The vast production of synthetic rubbers in the United States is almost exclusively based on emulsion polymerization. The procedure is moreover constantly being improved, with corresponding up-grading of the products. Dunbrook [9] has discussed American procedure.

The basic steps in the production of GR-S from butadiene and styrene are:

1. *Emulsification.* About three parts of butadiene and one part of styrene are fed into a soapy-water solution and emulsified by vigorous stirring.
2. *Polymerization.* The combining of the butadiene and styrene molecules begins, a catalyst is added, and the temperature is raised to accelerate the reaction.
3. *Coagulation.* The latex is removed from the polymerization tank and placed in another tank, after which sulphuric acid and a salt solution are introduced. The latex coagulates and rises to the surface of the tank.
4. *Collection.* The crumbs, or " flocs ", of rubber are skimmed off, washed thoroughly, drained, dried, and pressed into blocks for shipment to manufacturers of rubber goods.

The procedure adopted at the Buna works at Schkopau admirably illustrated the practical application of this method, for according to Ambros: [1]

> As the best method for polymerization of butadiene, for example, in making copolymers of the two components, butadiene and styrene, the technique of emulsion polymerization was evolved. It was important to know that materials such as butadiene and other chemical compounds such as styrene could be polymerized together because with this there came the possibility of making new technically valuable types of Buna. The most important type of Buna is of course Buna-S, but Perbunan which is the oil-resisting quality of Buna, is also a copolymer (of butadiene and acrylic nitrile).
>
> Thus the Schkopau plant was producing 300 tons per month of Nekal, the emulsifying agent, most of which was used in producing Buna S. Nekal is the sodium salt of butyl naphthalene sulphonic acid.

It must be quite evident to those familiar with synthetic rubbers that they have undergone remarkable improvement in recent years. This is almost entirely due to the benefits derived by the use of emulsion polymerization methods in their production. It has been found that in every case far superior products have been obtained by avoiding the production of massive polymerization products.

These emulsion processes, begun before the last war, were based almost entirely on analogy with rubber latex. With the sudden growth of interest in rubber latex in the 1920's, it was natural that there should be a recrudescence of interest in synthetic latices. As the knowledge and experience with emulsions has developed and grown side by side with the knowledge of rubber latex, so the emulsion method for polymerizing synthetic rubbers, has been developed to the stage when it has become commercially practicable. By 1930, for example, the Germans were already polymerizing butadiene in emulsion. Thus Heuck [15] described how this was achieved by heating the emulsion with hydrogen peroxide as catalyst for three days at 40° C., after which time a synthetic latex had been produced.

The position is roughly analogous to the change-over from wild uncultivated natural rubber to the carefully graded pleasant plantation rubber of to-day. Indeed, the availability of synthetic rubbers as latices enables the solid materials to be produced in a similar manner to that practised in the production of the commercial forms of natural rubber.

Advantages of Emulsion Polymerization. Polymerization in aqueous emulsion has numerous overwhelming advantages over any other procedure, perhaps, the most outstanding being that the reaction is always under control. There is little difficulty in handling the process and it may be stopped at any stage of the polymerization.

The procedure lends itself to the addition of other materials, either to facilitate the actual polymerization or to modify the properties of the subsequent synthetic elastic. The degree of polymerization is necessarily determined by the nature of the treatment used, i.e. the temperature and nature of the catalyst, and the time involved. In general the rate of polymerization is much more rapid when this method is used. This may be a function of available surface.

One of the great features of all emulsion processes is the absence of solvents which are invariably either toxic, inflammable or expensive. The process works at quite low temperatures and reaction is smooth and under control, there being no violent surges or other uncontrollable reactions. As a consequence there are no deleterious resinous by-products formed. In fact, emulsion polymerization eliminates most of the factors which have impeded particularly the commercial production of the synthetic rubbers. This value is further enhanced by the fact that successive batches of material do not differ in their characteristics.

No difficulty is experienced in preparing butadiene, isoprene, chloroprene, etc., as emulsions. Very concentrated emulsions can be

made, but 40 per cent. diolefine appears to be the most popular proportion. The final product is obtained as a finely divided suspension, or latex. The use of protective agents enables this to keep indefinitely. There is great scope for synthetic rubbers in the form of their respective latices. This parallels the growing application of rubber latex which in 1939 had reached a consumption of 30,000 tons in the United States alone.

The rapidly growing interest in natural latex was diverted to synthetic latices. The rate of development has been phenomenal. In 1943 synthetic latex containing about 300,000 lbs. total solids was made. In 1944 the amount had risen to 14 million lbs. In 1945 it rocketed to 34 million lbs. In 1946 it reached 55,400,000 lbs. and consumption is still increasing.

It is, of course, possible to obtain products which have been polymerized to an intermediate stage. In order to obtain the synthetic rubber in the solid form, generally regarded as most acceptable for processing, the final latex may be coagulated in exactly the same manner as rubber latex by the addition of acids and coagulent salts, etc.

All the familiar conditions associated with emulsions have been brought into play to deal with this problem of polymerization, e.g. the use of emulsifying agents, protective colloids, electrolytes, etc. Superimposed upon the factors necessary for the straightforward emulsification has been the addition of catalysts to promote polymerization, and also the addition of materials intended to modify the final products.

These include "modifiers" and also "stoppers" intended to inhibit after-polymerization.

A vast range of emulsifying agents has been employed in the production of synthetic rubbers. All the well-known soaps and wetting agents have been tried. Those most frequently encountered include sodium oleate, sodium stearate, a whole range of sulphonated mineral oils, organic sulphonic acids, saponin, etc. The Germans used Nekal, which is made from normal butanol, naphthalene, sulphuric acid and oleum. They also regarded mepasine sulphonate ($C_{12}H_{25}SO_3$) as one of the best emulsifying agents at all pH values. All the familiar colloidal materials employed in rubber latex work are encountered in the patents relating to synthetic rubbers. These, which include egg albumen, gum arabic, gelatin, glue, casein, milk, starch, dextrin, carrageen moss, are claimed to exert favourable effects on the emulsion, improving the stability during heat polymerization and reducing the time required. Being water-soluble materials they tend to exert an unfavourable influence on the water-resisting qualities of the final product.

The value of many of these additions is, to put it mildly, question-

able. However, it is only now with production on a large scale in full operation that effective weeding out of these materials is taking place.

Although polymerization in emulsion can be carried out without catalysts, the addition of these greatly speeds up the reaction. The most important reagents employed as in other forms of polymerization, and for plastics generally, are the oxidizing agents such as hydrogen peroxide, urea-peroxide, benzoyl peroxide, perborates, persulphates, percarbonates, ozonides, etc. Other types of catalysts include finely divided metallic oxides and salts of heavy metals, including manganese, lead, silver, nickel, cobalt and chromium. The presence of small quantities of halogen compounds such as carbon tetrachloride, hexachloroethane, trichloroacetic acid, etc., appear to have an all-round beneficial effect. This was described in another I.G. patent:[16]

One hundred and fifty parts butadiene by weight and 15 parts hexachloroethane are emulsified in a solution of 15 parts sodium stearate in 150 parts water. At ordinary or slightly increased temperature a substantially quantitative yield of synthetic rubber is obtained in 5 days. Without the hexachloroethane the yield is only 45 per cent. and cannot be substantially increased by prolonging the duration of the process.

Gerke[12] has stated that acid anhydrides such as acetic or benzoic anhydrides also appear to accelerate the rate of polymerization in the presence of inorganic peroxides.

TABLE 69. TYPICAL EMULSION REACTION MIXTURE

Butadiene	60 – 75
Styrene	40 – 25
Emulsifying agent	1 – 5
Polymerization catalyst	0·1– 1·0
Modifying agent	0·1– 1·0
Water	100 –250

From the plastics point of view, nearly every advantage claimed for production of synthetic rubbers by polymerization of diolefines in aqueous emulsions applies equally well for most synthetic resins. The trend is for their manufacture in this manner. The emulsification of the respective monomers presents no difficulties.

Patent literature contains many examples of satisfactory polymerization recipes. The following, from a U.S. patent, is a typical example:

Butadiene	7·5 grams
Styrene	2·5 grams
Isohexyl mercaptan	0·05 gram
Water	18·0 grams
Sodium oleate	2·0 grams
Ammonium persulphate	0·03 gram
Temperature	30° C.
Time	"Several days"
Yield	"Excellent"

An understanding of the function of each ingredient is essential. In the above example, the butadiene and styrene are the monomers, which, by copolymerizing, form synthetic rubber. The isohexyl mercaptan is described as a substance exerting a " regulating effect " or " modifier ", i.e. it possibly decreases the branching characteristics of the resulting polymer. Sodium oleate is the emulsifying agent, and ammonium persulphate acts as a polymerization initiator, also called a " polymerization catalyst ".

Starkweather and his colleagues [22] in a very comprehensive paper on many aspects of polymerization showed that the rate of polymerization in emulsion depended on the amount of catalyst. They showed, moreover, that increase beyond a certain amount of catalyst actually retarded polymerization. They treated 75 parts butadiene and 25 parts styrene for 16 hours at 60° C.

Ammonium persulphate %	Product yield
0	6
0·25	50
0·5	85
1	97
1·5	95
2	58

Conditions for Emulsion Polymerization. An excellent summary of the conditions required has been given by Mark and Rath.[18]

Our experience so far may, perhaps, be summarized in the following general way :

A series of components (between five and ten) are needed to build up the colloidal system in which the polymerization is expected to take place and to start and direct the reaction to its proper ending.

1. *The basic phase*, in which the emulsion is made This is always, or mostly, water (free from iron, lime, and organic impurities). It is always in excess and represents between 60 per cent. and 80 per cent. of the weight of the total system.

2. *The main monomer*—butadiene, vinyl chloride, etc.—to build up the backbone of the polymer to be produced. This will amount to about 60–80 per cent. of the final polymer or 15–30 per cent. of the emulsion.

3. *The additional monomers*—styrene, acrylic nitrile, acrylic esters, vinylacetate, etc.—which are present only if copolymers are to be produced. These will represent 24–40 per cent. of the weight of the final copolymer or about 5–15 per cent. of the initial colloidal system.

4. *The emulsifying agent* or agents, which enable us to produce colloidal dispersion of the monomers. Many different substances have been described and used and it seems that the actual choice of a special emulgator is of a certain importance for the success of polymerization. Aliphatic long-chain carboxylic and sulphonic acid salts, sulphonated long-chain alcohols and amines as well as aromatic alkylated sulphonic acid salts have been applied

with success. 0·2–2·0 per cent. of emulsifier, reckoned from the weight of the resultant polymer, are usually used.

5. *The stabilizer*, to prevent a premature precipitation of the emulsion. Various natural and synthetic protective colloids are recommended for this purpose, e.g. gelatine, glue, casein, starch, dextrines, methyl-cellulose polyvinylalcohol, etc. The usual amount of stabilizer is between 2 per cent. and 5 per cent. of the weight of the polymer.

6. *The regulator of surface tension*, the action of which cannot yet be clearly defined. It seems, however, that these substances have to be present to obtain and maintain the most favourable average particle size of the emulsion and to narrow down as much as possible the distribution curve of the size of the dispersed particles of the monomer or the mixture of monomers. Aliphatic alcohols of medium chain length C_5 to C_8 seem to serve this purpose best, but aromatic alcohols and amines have also been recommended. They amount to between 0·1 per cent. and 0·5 per cent. of the polymer.

7. *The catalyst*, of which the main action is presumably the acceleration of the formation of polymerization nuclei without affecting the propagation process. It seems, however, that most substances which catalyse the starting reaction act similarly towards the cessation reaction and thus the addition of too much catalyst may result in a polymer of low molecular weight. Oxygen ozone, hydrogen peroxide, organic peroxides and ozonides, persulphates, percarbonates, perborates and similar substances act as catalysts; they usually amount to between 0·1 per cent. and 1·0 per cent. of the weight of the resultant polymer.

8. *The regulator*, to direct the polyreaction and, presumably, to act mainly as an " anti-knocking " agent, avoiding or cutting down branching and cross-linking processes during the reaction. Very little is actually known about the action of these substances. Experience has shown that chlorinated aliphatic hydrocarbons such as carbon tetrachloride, ethylene dichloride, and hexachloroethene and similar aromatic compounds have a beneficial influence on the reaction, if about 2 to 5 per cent. of the weight of the polymer is added.

9. *The pH adjuster or buffer.* Most emulsions are very sensitive to the hydrogen-ion concentration. The particle size and its distribution curve, the actual mechanism of the reaction and the stability of the final synthetic latex sometimes depend largely on the maintenance of the proper *p*H. Normal buffers such as phosphates, carbonates, acetates, etc., are usually applied in appropriate amounts (2–4 per cent. of the weight of the polymer).

The above list shows that the mechanism of an emulsion polymerization is quite complicated.

They considered the action of emulsion polymerization to be polymerization of the drops of the monomer proceeding inwards from the interface with the medium. Fikentscher [11] considered that the part dissolved in the aqueous solution polymerizes, after which more was dissolved from the droplets. He based this on the fact that saturated solutions of vinyl monomers in water gradually formed emulsions of insoluble polymers. Staudinger [23] considered that polymerization in emulsion strongly favours the formation of many activated spots on

the surface of particles which give rise to a particularly reactive nucleus for promoting chain reactions and the process of polymerization is therefore accelerated.

Soaps in Synthetic Rubber. The nature of the soap and emulsifying agent employed in synthetic rubber production plays a profound part in deciding the properties of the final product.

In emulsion polymerization the soap and the water perform definite jobs. According to Semon [21] most evidence suggests that polymer particles originate by polymerization of the monomer molecules dissolved in the aqueous phase or made soluble by the soap. Polymer growth then continues at interfaces where soap is concentrated as micelles or adsorbed on the surface of the polymer particles. This is supported by the fact that water-soluble initiators of polymerization such as hydrogen peroxide, or potassium persulphate, are more effective than oil-soluble materials such as benzoyl peroxide.

Soaps have a profound influence on the initiation and the speed of polymerization. Efficiency is of the same order as their solubilizing action on the polymers. Thus many synthetic detergents are much more efficient than fatty acids in emulsifying the monomers, but are useless for initiating polymerization. In emulsion polymerization the rate of polymerization is roughly proportional to the concentration of fatty soap. It is thought that the rate of polymerization is proportional to the amount of monomer solubilized by the soap. The soap actually participates in the initiation of polymerization and affects the emulsification of the resulting polymer.

Harkins [14] has outlined the progress of emulsion polymerization. It starts actually in the soap micelles (colloidal aggregates). These are rapidly depleted during polymerization because the polymer particles, as they form, adsorb a layer of soap from the water later. This causes solution of the micelles. When a mass of polymer equal to two or three times the mass of soap has been formed, no micelles are left in the aqueous phase. Relatively few new particles can form and polymerization proceeds in the polymer particles which grow larger. Monomer dissolves in these particles so that long before polymerization is finished no more emulsified monomer remains in the water phase. Thus the latex will barely foam. Long before polymerization is complete owing to the fact that soap has been removed from the aqueous phase the polymer particles are only partly covered with soap and tend to become unstable. For stabilization more soap or surface active material must be added. Where latex is to be directly converted to solid rubber no further addition is necessary. In coagulation with dilute acids or alum, the soap is converted to fatty acid or aluminium

soap. These can be left in most rubbers. In other cases they can be washed out with alkali.

Many fatty acids can successfully be employed in polymerization. Palmitic acid, stearic acid and oleic acids are very effective. Myristic acid is the most effective one in making nitrile rubbers. The large-scale production of GR-S makes use of mixed hydrogenated tallow acids.

Soaps have a very marked influence on the technical behaviour of the final rubber. American experience has established this beyond any question. Thus GR-S with fatty acid is deficient in tack and hard to process. It was found that the use of the sodium salt of disproportionated rosin acid produced the material known as GR-S 10, which could be processed more readily, had greater tackiness, and when vulcanized showed better physical properties. This is in large-scale production.

Until 1935, the I.G. used oleic acid. They then replaced part of the oleic acid by Nekal (sodium isobutyl naphthalene sulphonate). They then changed to 3 parts linoleic acid (from linseed oil) and 4·5 parts Nekal per 100 parts Buna S. This rubber was easier to process and had improved physical properties. The lack of linseed oil forced them to use Nekal and a small amount of the sodium-salt of a fatty acid obtained from the Fischer-Tropfsch process. The resulting rubber proved to be far superior, being still easier to handle and having even better physical properties. This is the material they call mersolat.

GR-S Formulation

	Parts by weight
Butadiene	75
Styrene	25
Soap	5
Mercaptan	0·5
Potassium persulphate	0·3
Water	200

Buna S3 Formulation

	Parts by weight
Butadiene	70·0
Styrene	30·0
Nekal	3·0
Sodium-paraffin fatty acid	0·5
Sodium hydroxide	0·4
Potassium persulphate	0·4
Diproxid	0·06
Water	106

Regulators of Polymerization or Chain Straighteners. These are compounds which are present in small amounts during polymerization.

The function of the regulator in polymerization is to keep the polymer chain to form as long straight chains and to prevent it from branching and cyclizing. Consequently they have a profound influence on the plasticity and solubility of the resulting polymers. It is found that different regulators give rubbers having various degrees of hard-

ness. It is also found that the *p*H of the emulsion has an important influence on the effect.

In American practice the favoured regulators are mercaptans, the chief one being tertiary dodecyl mercaptan, while tertiary mercaptans are also used. The favoured material employed by the Germans is diproxid. The straightening effect is only achieved by adding small amounts of the regulator at equal intervals during polymerization. For high quality polymers the K value should be high and maintained as near constant as possible throughout polymerization. Some cynics suggest that these materials merely function as peptizers.

Apart from materials already mentioned, large amounts of chlorinated hydrocarbons up to 20 per cent. will also function.

Stoppers or Chain Terminants. When the desired degree of polymerization has been attained, it is necessary to stop further polymerization and to stabilize the rubber. This is usually achieved by adding an emulsion of phenyl-β-naphthylamine, the amount being about 2 per cent. on the rubber. Another stopper is hydroquinone. An important practical feature is that the stopper must be added at the end of the process and away from the reactors. If added during polymerization it acts as a strong poison.

Predominance of Emulsion Methods for Synthetic Rubbers. As already suggested there is strong evidence to presume that emulsion polymerization predominates in the United States and Germany, and that all other methods have been pushed into the background. The modern large-scale plants have been based on the use of this method. According to Stöcklin:[24]

It was clear from the beginning that polymerization in emulsion would be technically more valuable if it were possible to obtain a product equal to or even inferior to the sodium polymerizate. It soon became clear that in the case of the emulsion polymerization of butadiene the cyclization in the polymerization was much greater than that found in the products obtained by the sodium polymerization process. . . . Further work showed that less cyclized products with better properties from the rubber technologist's point of view were obtained if the mixtures of butadienes hydrocarbons were polymerized in emulsion. Thus Perbunan is a mixed polymerizate of butadiene and acrylic acid nitrile.

Unmistakable evidence that the emulsion process of polymerization is undoubtedly the best is the fact that the latest plants constructed in the United States and in Germany work on this system. The enormous works at Schkopau were built after the successful career of a pilot plant working the emulsion process.

The actual changes employed in the production of the various Buna Rubbers illustrate emulsion polymerization.

TABLE 70

Material	Buna S	Buna SR	Buna SS	Buna S3
Butadiene	68	68	47	68
Styrene	32	32	53	32
Nekal	2·85	2·85	3·2	3·1
Linoleic acid	2	2	2·5	—
Paraffin fatty acid	—	—	—	0·5
Caustic soda	0·44	0·44	0·55	0·32
Diproxid	—	—	—	0·09
Potassium persulphate	0·46	0·46	0·61	0·45
Water	120	120	182	105

Paraffinic fatty acid was prepared by oxidation of paraffin obtained from Fischer-Tropfsch plants, consisting of a range of C_{10} to C_{15} fatty acids. These materials came into use when linoleic acids became scarce.

Diproxid. Diproxid is the name given to di-isopropyl xanthate. This is made by reacting together carbon-disulphide, isopropyl alcohol, and potassium hydroxide. These yield potassium isopropyl xanthogenate. When heated with sodium hydrochlorate a white precipitate is obtained which is diproxid. Its function is to act as a chain straightener in making Buna S3, i.e. it tends to prevent cyclization, acts as a regulator of the molecular structure, and gives an easier processing material.

Rapid Polymerization. Polymerization processes are still rather lengthy. There is still considerable scope for reducing the time. In this way the output of existing plant could be very considerably augmented. The fact that most polymerization is now carried out continuously to some extent offsets the lengthy operation, but more rapid polymerization would obviously have many advantages. The American processes for making GR-S take about 14 hours at 50° C. This is much more rapid than the German procedure. Schkopau polymerization took about 30 hours at 50° C.

Latterly new methods have been developed which accelerate the process of polymerization in a remarkable manner. These methods investigated in the United States and in Germany have only just reached the large-scale production stage. Leading products are Philprene and Ultipara. They are known as Redox systems. The principle involved is to use a combination of oxidizing agents and a reducing agent in the presence of small amounts of oxygen. The amount of oxygen is critical, because above certain limits it acts as a definite poison. By means of these methods polymerization can be carried out in as little as 10 minutes at 50° C. or in 24 hours at 10° C. The ability to carry out polymerization at low temperature in a reasonable time is most significant.

Rubbers obtained at low temperature appear to be much superior *to present types.*

According to the German methods effective reducing agents included acetol, which is $CH_2OH\ CO\ CH_3$, or potassium persulphate in quantities of about ½ per cent. of the monomers. One German procedure employs the oxygen available from the air dissolved in the water employed during polymerization using *Mersolat* as the reducing agent. Operating at a *p*H 2 to 5 polymerization was effective in about 10 minutes at 50° C.

It was suggested that small amounts of oxygen acted by formation of the group —C C— but that larger amounts formed a different group

O
—C– C— which is inactive. Hydrogen peroxide is not very effective
| |
O—O

as oxidizing agent. While benzyl peroxide is effective its use has numerous disadvantages. Most interesting redox agent is cumene hydroperoxide. From the commercial point of view the most favoured material is potassium persulphate.

Vandenberg and Hulse [25] have described a typical American redox formulation.

	Parts by weight
Butadiene	75
Styrene	25
Denatured rosin soap	5
Sodium hydroxide	0·061
Mercaptan	0·5
Cumene hydroperoxide (initiator)	0 17
Fructose (reducing Agent)	0 5
Ferric pyrophosphate	1 5
Water	180

In case it has not been made quite clear, the polymerized product is obtained still in the form of an emulsion or latex. Some of the properties of Buna latices were described by Baechle.[2] They resemble rubber latex in many ways. The particles in dispersion are negatively charged, and the stability is of a similar order. The particles are spherical, unlike the rubber particles, and are about one quarter the size, i.e. of the order of 0·1 microns in diameter. Buna latex coagulates to small flakes in contrast to the solid coagulum formed by rubber.

Synthetic latices are stabilized with alkali soap, etc., and are sufficiently stable to be utilized for all processes where natural latex is used, e.g. spreading, dipping, spraying, impregnation, electro-

deposition, foaming, and so on. They are handled by the same methods as used for natural rubber latex. They are able to form *tough, coherent, elastic films.*

With recent advances in polymerization methods it has become possible to prepare concentrated latices in the actual reaction vessel. The normal concentration methods, e.g. by evaporation, are thus being eliminated. Creaming and centrifuging are not very satisfactory.

Buna-N Latices. Buna-N latices are slightly alkaline and contain very little soapy substances. There is no tendency for bacterial growth in these latices since they are free from albuminous protective colloids. Buna latex particles carry a negative electrical charge and are therefore discharged by H-ions and coagulated. As in the case of rubber latex it is possible to change the electrical charge of the Buna particles from negative to positive. The solid content of Buna latex is generally 30 per cent. It is difficult to cream or centrifuge Buna latex because the particles are much smaller than normal rubber particles.

According to Mueller [19] suitable coagulants and creaming agents for Buna latices include the following. They are the same as operate for rubber latex.

TABLE 71. CREAMING AGENTS FOR BUNA LATEX

Coagulants	Creaming agents
Acetic acid	Caraya gum, Locust bean gum, Gum tragacanth: 0·1–0·5% on dry rubber
Formic acid	Iceland moss
Calcium chloride	Alkaline solution of alginic acid
Calcium acetate	Caustic soda and other alkalies
Calcium nitrate	Irish moss
Calcium formate	Ammonium alginate (one of the most effective, the effect is accelerated by heating the system to about 60° C.
Zinc chloride	
Ammonium acetate	
Acetone	
Methyl alcohol	
Alum	

When polymerization has been finished the Buna latex is decanted from the unreacted part. Any surplus of acrylonitrile can be distilled and recovered. Because of the high stability of the Buna latices, few coagulating agents are sufficiently effective to be of practical importance. Almost immediate .coagulation is effected by barium chloride, ethyl alcohol, hydrochloric acid, sulphuric acid, acetic acid. Aluminium chloride and ferric chloride have a tendency to flocculate the Buna latices. Calcium chloride, calcium nitrate, tin chloride, calcium acetate, zinc chloride and magnesium chloride precipitate the Buna in the form of a gel. Table 72 shows the minimum amount of coagulent necessary for precipitating 100 parts of Buna-N latex.

TABLE 72. COAGULANTS FOR BUNA LATEX

	Parts
Aluminium chloride	1·5
Ferric chloride	2·0
Calcium chloride	2·5
Barium chloride	5·2
Acetone	98
Ethyl alcohol	110

Heat sensitizing and gelling agents do not appear to affect Buna latices. The hardness or toughness of the final Buna-N or -S can be controlled to some extent in their preparation. In practice other methods are necessary. Buna-S can be heat-treated or peptized with different chemicals and any degree of softness can be obtained.

General Activity with Emulsions. Although the Americans and the Germans have made a special feature of butadiene polymerization from emulsions, there has been a certain amount of activity elsewhere. A great deal has been heard about Soviet efforts to make synthetic rubbers by emulsion.

It would appear that emulsion polymerization is beginning to register its importance. For example, Dogadkin, Beresan and Lapuk [8] claimed to polymerize butadiene compounds as aqueous emulsions in the presence of tautomeric substances such as diazoamino compounds.

Polymerization of butadiene in emulsion has been carefully examined by U.S.S.R. workers.[3] They prepared the latex and considered all its properties. They also considered the effects of stabilizers, the media, and the influence of catalysts on the rate of polymerization. Thus dimethyl butadiene alone polymerized in 40 days at 70° C. yielding 18 per cent. of polymer. In emulsion it took only 8 days. Butadiene without catalysts took 15 days to polymerize in emulsion, but months in the ordinary state.[4] They considered that polymerization was a chain reaction.

Synthetic rubber-like materials have been made from emulsions in this country. Thus Habgood and Morgan [13] polymerized an emulsion containing a mixture of butadiene and from 25 to 100 parts of methyl methacrylate in the presence of from 5 to 30 parts carbon tetrachloride.

Neoprene is Produced by Emulsion Polymerization. The best-known elastomer is, of course, neoprene. This is based on a polymer of chloroprene, or 2-chloro-1,3-butadiene. It was the first commercial synthetic rubber, appearing on the market in 1930, and is the most widely used. As in the case of the Buna rubbers, there have been very marked improvements in the quality of neoprene during recent years. These changes have largely been associated with

improvements in the technique of polymerization, most notably by the introduction of emulsion methods.

The production of neoprene came about as a consequence of the work carried out by Nieuwland [20] on the polymers of acetylene. In particular he developed a method for the commercial production of monovinylacetylene by passing acetylene through cuprous chloride solution. This work was followed up by an intensive and thorough investigation, sponsored by Du Pont de Nemours, into the possibilities of utilizing monovinyl-acetylene as a basis for producing synthetic rubber. Carothers, Williams, Collins and Kirby [5] were able to convert monovinylacetylene into chloroprene by treatment with hydrogen chloride, using cuprous chloride as catalyst. They also determined the conditions for making chloroprene polymerize to yield commercial products. This very brief description does scant justice to some of the most brilliant work in chemical history.

Like isoprene, chloroprene is capable of yielding rubber-like polymers, but owing to the presence of chlorine in the butadiene system, which renders the molecule markedly polar, it polymerizes far more rapidly than does isoprene. The influence of a halogen atom in an unsaturated system on the rate of polymerization is well shown by comparing ethylene ($CH_2 : CH_2$) with vinyl chloride ($CH_2 : CHCl$). Vinyl chloride polymerizes not only more readily but to a far higher degree than does ethylene.

Chloroprene is a colourless liquid which polymerizes with ease. It tends to change spontaneously on standing. If allowed to stand for ten days it forms a copolymer known as the μ- form, which is a resilient mass, insoluble in solvents, and somewhat similar in character to vulcanized rubber.

If polymerization is interrupted, a lower polymer is obtained (α-polychloroprene), which is soft, plastic and soluble in solvents, resembling unvulcanized rubber in many ways. This is the basis of the neoprene of commerce.

In the past there have been features of neoprene that were open to criticism, notably the bad odour and the dark colour. In the case of neoprene it has been clearly evident in recent years that these grounds for criticism have been almost eliminated. Products can now be made in the most delicate of pastel shades, having virtually no odour.

The newer improved types are prepared by emulsion methods. Once again it should be observed that direct bulk polymerization processes tend invariably to yield by-products that are deleterious—for it becomes more strongly emphasized that the disadvantages in polymers are chiefly due to such by-products.

The polymerization of chloroprene in emulsions gives interesting results. When emulsified, chloroprene changes to the μ- polymer more quickly than when in the massive condition, the rate of polymerization being apparently at least twenty times as rapid as that of undispersed chloroprene. If chloroprene is emulsified in a solution of sodium oleate and the emulsion is allowed to stand, polymerization is so vigorous that the temperature begins to rise in about 30 minutes and may quickly reach the boiling point of chloroprene unless cooling is applied; polymerization is complete in 2 to 8 hours at room temperature. The product, which corresponds to a vulcanized latex, may be stabilized by adding a little ammonia, which neutralizes the small amount of free acid which is formed during polymerization and which would otherwise bring about gradual coagulation. Latex thus prepared is fluid so long as the concentration of polychloroprene is not more than 55 per cent. The average particle diameter is only 0·126 μ. In natural latex the particle size ranges from 0·5 to 3 μ.

The use of a number of different emulsifying agents with chloroprene has been studied by Williams and Walker.[27] Turkey-red oil, casein dispersed with sodium hydroxide or acetic acid, triethanolamine stearate, and sodium stearate all give emulsions in which chloroprene polymerizes completely within a few hours and in which the particle size is similar—viz., 0·1 to 1 μ. Carrageen moss, on the other hand, gives an emulsion which, although the particles are similar in size, does not lead to acceleration of the polymerization, the material separated from the emulsion being the plastic, α- polymer. If sodium stearate sufficient to provide a mono-molecular layer is added to a carrageen moss emulsion of chloroprene, polymerization proceeds rapidly. The nature of the interfacial layer is considered to have an important influence on the rate of polymerization.

In a Du Pont patent some of the mechanics of emulsion polymerization are described.[10] Although neoprene is not directly mentioned, the method seems likely to have a bearing on the production. Emulsions of styrene, acrylic acid nitrile, etc., containing catalysts, are polymerized by passing them through tubes having diameters not greater than 2 inches and of sinuous form having acute bends. The velocity of flow is sufficient to cause turbulence. The tube is heated to effect polymerization.

The following laboratory method illustrates how the emulsion process functions in the case of neoprene.

400 gm. chloroprene is added, with vigorous stirring, to 400 gm. water containing 5 per cent. sodium oleate. The resulting emulsion is kept at 10° C. for a period of between 24 and 48 hours, depending on

the degree of polymerization desired. A little ammonia is added to counteract any acidity.

Solid neoprene is obtained from the synthetic latex in the same way as rubber is obtained from latex, by coagulation with acids and multivalent salts. Light-coloured, almost odourless products are obtained. Quite clearly neoprene becomes available as latex, a fact which obviously widely increases the scope of the material.

According to Dales,[6] neoprene latices may contain up to 50 per cent. of total solids, which upon evaporation or coagulation and subsequent washing, yield commercial neoprene. As in the case of rubber latex, these latices may be compounded and loaded with fillers, and films from them may be vulcanized.

The monomer 2-chloro-1,3-butadiene, is emulsified as spherical particles of from 2 to 4 μ diameter. During polymerization these change into particles of only 0·1 μ diameter. The particles are in such violent Brownian motion that there is no tendency for them to settle, an action which would be comparable with the creaming of rubber latex (neoprene has specific gravity of 1·25, while that of rubber is 0·93).

Following on their application of the emulsion polymerization technique to the butadienes, the I.G.[17] have extended the process to substituted butadienes such as chloroprene. They polymerized 2-chloro-1,3-butadiene in the presence of organic sulphur containing compounds that are soluble in the monomer such as dialkyl xanthogen disulphides. They extended the process to polymerize chloroprene with other monomers such as styrene and acrylic nitrile. In one example 10 parts acrylic nitrile together with 180 parts chloroprene and the catalyst were emulsified in a soap solution prior to emulsification.

Synthetic Latices. Many synthetic elastomer latices have attained prominent commercial importance; among them are latices from copolymers of butadiene and styrene; copolymers of butadiene and acrylonitrile, polymers of chloroprene and polyethylenepolysulphide.

Synthetic latices have many colloidal properties by which they can be compared with *Hevea* latex. Generally both *Hevea* and synthetic latices can be described as stabilized suspensions of microscopic negatively charged hydrocarbon particles small enough to exhibit Brownian motion. In contrast to *Hevea* latex, which is stabilized with naturally occurring protein, synthetic latices are usually stabilized with alkali soaps or other surface-active agents. These differences in stabilizers have important bearing on differences in properties of the two types of latex.

Both types exhibit structural viscosity characteristic of colloidal systems and are coagulated by acids, multivalent metallic ions, and certain organic solvents. The synthetic varieties are much more stable to mechanical agitation than *Hevea* latex. Chemical stability is influenced by so many individual factors that a direct comparison cannot be conveniently made. However, it is sufficient to say that the chemical stability of the synthetic latices is high enough to render them satisfactory for compounding and use in the latex process.

In general, the particles of synthetic latices are smaller and more uniform in size than those of the natural latex, being in the range of 0·1 micron in diameter. However, recent polymerization techniques have introduced a measure of particle size control so that, to a degree, latices of predetermined particle size can be made. The smaller particle sizes of synthetic latex affect their viscosity and other properties. Synthetic latices are therefore less susceptible to spontaneous creaming or settling than *Hevea* and therefore do not lend themselves to commercial centrifugal concentration, although the viscosity of the concentrate and differences in gravity between the polymer and serum phases are important additional factors.

In compounding consideration must also be taken of the higher adsorption of surface active materials on the small particles of synthetic latices. The high adsorption of stabilizers by the synthetic latices must also be taken into consideration in making blends as with *Hevea* latex. Cases have been observed where the high adsorption tendencies of the synthetic phase have destabilized and coagulated the compound. Theoretically, the smaller synthetic latex particles should give better impregnation of fibres.

Until recently, synthetic latices were usually produced in concentrations from 25 to 50 per cent. total solids. Higher concentrations were produced by evaporation or by creaming with ammonium alginate or similar materials. By creaming, concentrates approaching 60 per cent. total solids can be obtained; while by evaporation, creams considerably in excess of 60 per cent. are being produced commercially.

Recent advances in polymerization techniques have made it possible to produce several latices at high solids contents directly in the reactor during polymerization, and it is probable that except for unusually high solids contents most synthetic latices will eventually be polymerized at concentrations high enough for direct use, thus eliminating the supplementary concentration step entirely.

Most synthetic latices show slower drying characteristics and higher water adsorption than *Hevea* because of their high soap content.

For practically all of the processes normally employing natural latex

one or more of the synthetic types has been adapted with some degree of success. This applies to processes employing casting, spreading, spraying, dipping, electro deposition, extrusion, foaming, impregnation, and gelation.

The degree to which the synthetic latices are adaptable to latex processes are to a great extent dependent on their ability to form tough, coherent, and elastic gels and films, as is the case with *Hevea* latex. In general, nearness of the approach of synthetic latices to perform this function is a measure of their adaptability to existing latex processes.

The physical and chemical properties of the films formed from the synthetic latices follow roughly the characteristics of the pure gum milled film of the same polymer. As with *Hevea*, reinforcing-type pigments do not reinforce synthetic latex films except in some very special cases.

Considering the relatively short time during which intensive effort has been centred on synthetic latex, the progress has been remarkable. Continued research will undoubtedly produce synthetic latex equal or superior to the natural varieties. With the unlimited possibility of tailor-making latices to fit specific uses, advantages can be taken of the properties of special synthetic rubbers such as solvent resistance, resistance to deterioration by ageing, and fire resistance as well as other properties still unknown resulting from introduction of entirely new polymers.

GR-S Latices. The following three types of GR-S latex have already been established:

GR-S LATEX, TYPE I. This latex is the same as the latex from which standard GR-S is made by coagulation and drying and contains a butadiene-styrene ratio specified for standard GR-S.

GR-S LATEX, TYPE II. This latex is the same as Type I except that the antioxidant is omitted.

GR-S LATEX, TYPE III. This latex is made by charging approximately equal parts by weight of butadiene and styrene in a polymerization formula. This latex does not contain antioxidant or other stabilizer.

GR-S Latex. The leading type of synthetic latex, GR-S latex type III, has the following characteristics:

Colour	Brownish-white
Total solids	37 per cent.
S.G.	0·98 at 20° C.
*p*H	11·8
Particle size	Less than 0·5 μ

The ordinary GR-S with its proportion of 75 butadiene to 25 styrene has not been found to give a very satisfactory latex. The latest types are therefore based on a 50 : 50 ratio. It is stabilized with potassium rosinate.

This latex behaves like natural rubber latex in many ways. It can be concentrated by creaming or by evaporation. Films can be formed by air drying or by the use of coagulants. The films in general do not appear to be as good as those from natural latex. They can be vulcanized. They can also be mixed with rubber latex. These and other modifications are considered later.

One consequence of the use of emulsions in synthetic rubber production has been the enormous demand created for auxiliary chemicals. Vast quantities of emulsifying agents, fatty acids, mercaptans, and so on, have been required.

TABLE 73. U.S. SYNTHETIC LATEX PRICES, JUNE, 1948

Chemigum Latex 101	0·37–0·40 cents per lb. solids
Hycar latex OR 15	0·455–0·50
OR 25	0·385–0·46
OS 10	0·40–0·435
Neoprene Latex :	
Type 60	32–37
571	29–37
572	30–38
601	32–40
700	30–38
842	29–37
Perbunan :	
Type H (55 per cent.)	38–42

REFERENCES

[1] AMBROS, *Kunststoffe*, 1939, **29**, 166.
[2] BAECHLE, *Gummi Ztg.*, 1937, **51**, 719.
[3] BALANDINA, BERESAN, DOBROMYSSLOVA, DOGADKIN and LAPUK, *Bull. Acad. Sci. U.S.S.R.*, 1936, **397**, 423.
[4] BERESAN, DOBROMYSSLOVA and DOGADKIN, *ibid.*, p. 409.
[5] CAROTHERS, WILLIAMS, COLLINS and KIRBY, *J. Amer. Chem. Soc.*, 1931, **53**, 4203.
[6] DALES, *India Rubber World*, 1940, **103**, 102.
[7] DINSMORE, U.S.P. 1732, 795/1929.
[8] DOGADKIN, BERESAN and LAPUK, U.S.S.R.P. 46,354/1939
[9] DUNBROOK, *India Rubber World*, 1947, **117**, 203.
[10] Du Pont de Nemours, B.P. 518,657/1940.
[11] FIKENTSCHER, *Angew. Chem.*, 1938, **51**, 433.
[12] GERKE, U.S.P. 1,854,186/1932.
[13] HABGOOD and MORGAN, B.P. 511,838/1939.

[14] HARKINS, *J. Chem. Phys.*, 1945, **13**, 38.
[15] HEUCK, G.P. 558,890/1927.
[16] I.G., B.P. 349,499/1931.
[17] —— B.P. 512,458/1939.
[18] MARK and RATH, *High Polymer Reactions*, New York, 1941, p. 81.
[19] MUELLER, *India Rubber World*, 1942, **106**, 34.
[20] NIEUWLAND, *Science*, 1922, **56**, 486.
[21] SEMON, *India Rubber World*, 1947, **116**, 63.
[22] STARKWEATHER and Collaborators, *Ind. Eng. Chem.*, 1947, **39**, 210.
[23] STAUDINGER, see Koch, *Ind. Eng. Chem.*, 1940, **32**, 464.
[24] STÖCKLIN, *Trans. I.R.I.*, 1939, **14**, 51.
[25] VANDENBERG and HULSE, *Ind. Eng. Chem.*, 1948, **40**, 932.
[26] WHITBY and KATZ, *Ind. Eng. Chem.*, 1933, **25**, 1340.
[27] WILLIAMS and WALKER, *Ind. Eng. Chem.*, 1933, **25**, 199.

PART III

TECHNOLOGY OF SYNTHETIC ELASTIC MATERIALS

PART III

INTRODUCTION

Before beginning the next chapter, the technology of the various synthetic elastic materials must be discussed with reference to rubber technology. Consequently the terms of reference and procedures adopted with rubber are employed in these instances. For a full consideration of rubber technology the reader is referred to any text-book on the subject.[1, 2, 3] However, it seems desirable to explain some of the terms and abbreviations that may be employed.

The chief characteristic of rubber compounds which has been singled out as a standard for comparison is the *tensile strength at*

TABLE 74. SOME PHYSICAL CONSTANTS OF NATURAL RUBBER [4]

	Pure rubber	Commercial rubber	Soft vulcanized 20% S	Hard rubber 32% S
Density	0·9060	0·911	0·923	1·173
Specific heat Cals. per degree	0·449	—	0·510	0·341
Heat of combustion Cals. per gram	10820	—	10630	7920
Refractive index n_D	1·5190	1·5190	1·5364	1·6
Dielectric constant (at 1000 cycles/sec.)	2·37	2·45	2·68	2·82
Power factor (at 1000 cycles/sec.)	0·0016	0·0018	0·0018	0·0051
Conductivity mho/cm	23×10^{-18}	420×10^{-18}	13×10^{-18}	15×10^{-18}

break, with which is coupled the *elongation at break*. The abbreviations T_B and E_B respectively are employed for these. While these quantities serve as a convenient measure for the ultimate tensile properties of the material under consideration, yet they have little relation to the behaviour of the material under service conditions. A much more realistic appreciation is obtained from the *modulus* of the material, which is in effect the tensile strength at some predetermined elongation, e.g. the tensile strength at an elongation of 300 per cent. The modulus is really an indication of stiffness. A high modulus denotes a stiffer, more rigid material, while a low modulus indicates a soft yielding product. The abbreviation M_{300} is employed to refer to the modulus at 300 per cent. elongation. It is evident that this will give an indication

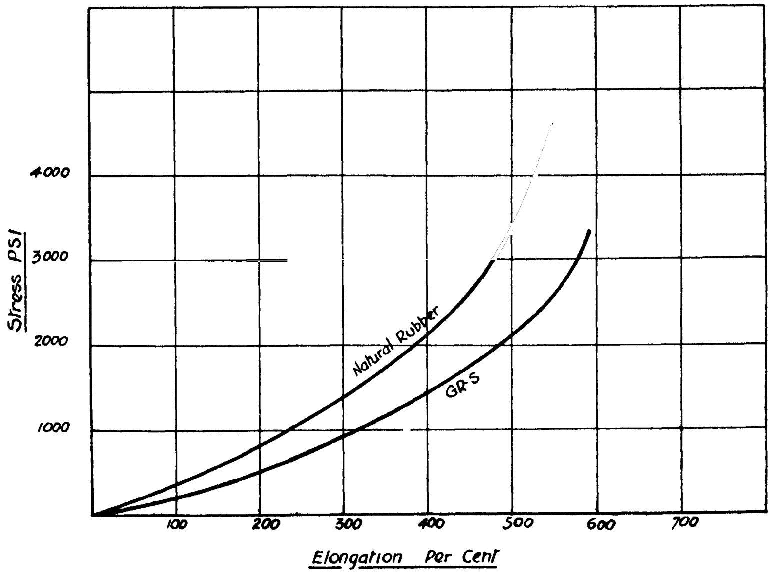


FIG 48—Stress-Strain Curves for Rubber and GR-S.

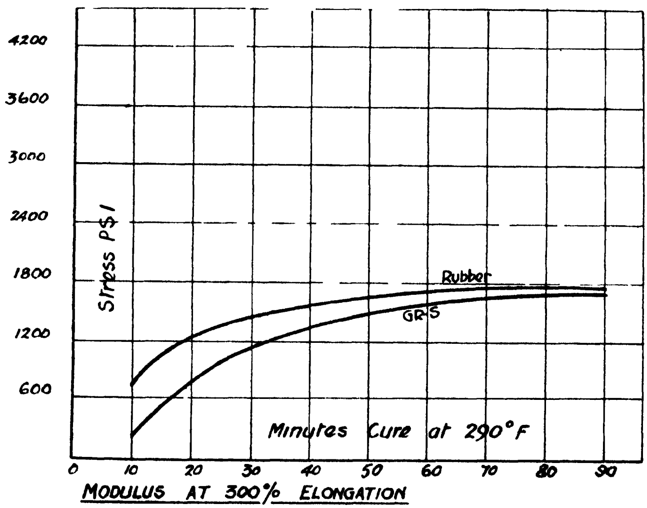


FIG. 49.

of the behaviour of any elastic material at the comparatively low elongations of most service uses.

Vulcanization of course refers to the heat treatment of a material whereby it is changed from the plastic to the elastic condition. The process is referred to technically as the "*cure*". The question of the state of cure, or vulcanization is technically of great importance. As the time of vulcanization of a product is increased, so the tensile strength increases until it reaches a maximum value. In the case of rubber where materials have been undercured, the tensile and other properties are inadequate; notably the permanent set is excessive;

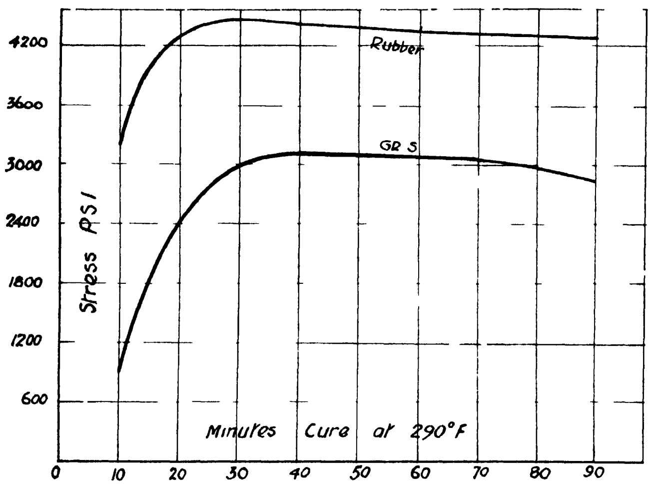


FIG 50—Tensile Strength at Different Cures

while where they have been overcured the ageing properties are bad and the material tends to become "short". Consequently, the optimum technical cure is generally sought. In this connection the term "*plateau effect*" is encountered. This refers to rubber compounds where the nature of the vulcanization, as modified by some specific accelerator, is such that the tensile properties during vulcanization tend to reach a maximum, and thereafter instead of falling off rapidly are maintained over a period of time. Thus if a rubber compound vulcanizes to give maximum tensile properties in 30 minutes at 140° C., then with an accelerator which gives a plateau effect the properties of the product obtained in 25 minutes will not be appreciably different from those obtained in 35 minutes. Consequently any cure during that period of time will give a satisfactory material, and as a

corollary the material will not be so sensitive to the vulcanizing conditions. The illustration shows why this is referred to as a plateau effect.

Accelerated ageing results are obtained by standard procedures. Heating in a Geer oven in air at a fixed temperature of 70° C. for a period simulates one type of ageing. Treatment in a Bierer-Davis oxygen bomb under high pressure of oxygen and at high temperature simulates another form of ageing. The tensile properties are taken as a measure of whatever changes may have occurred.

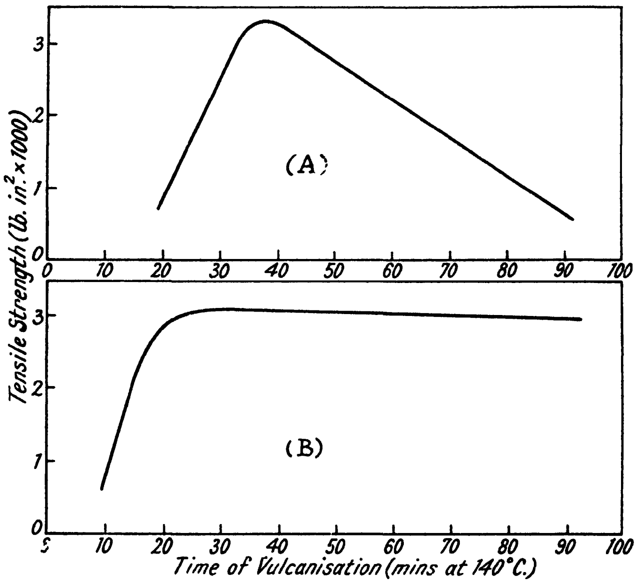


FIG. 51.—Plateau Effect.

Hardness, which is referred to by the abbreviation H, is generally measured by use of the Shore penetration instrument or with the British Standards Hardness Tester.

Other properties such as *abrasion resistance*, *tearing resistance*, *flexing resistance*, etc., are not yet standard procedures, and reference is made wherever necessary to the specific procedure adopted.

The degree of *permanent set* affords a test which is of great importance in connection with synthetic elastic materials as interpreting the extent to which they possess elastic qualities. This gives information as to what extent a product remains distorted after being subjected to stress. A sample is stretched to a definite extent, is allowed to stand for some time, after which the tension is relaxed, and the sample

is allowed to retract. The percentage increase in length is the permanent set.

Resilience is one of the most characteristic features of elastic materials, and in this respect rubber has not yet been equalled by any synthetic product. The snap or nerve of a product is a measure of this property. Actually of course, in use the material is subjected to comparatively small extensions or compressions carried out very rapidly, as in the case of a tyre. It is the resilience in such circumstances which is of importance. It is measured by the amount of energy returned by the rubber. One of the most widely used methods for doing this is to determine the height to which a steel ball or a pendulum will rebound after striking the sample. The percentage of rebound gives a measure of the impact resilience.

Hysteresis is of great technical importance. It is a measure of how much energy is lost in extension and retraction in the form of heat. In this instance, too, rubber has a lower hysteresis than any of the synthetic materials. It is of outstanding significance when there are rapid cycles of extension and retraction such as occur in a tyre tread. High heat losses may cause overheating of the tyre. On the other hand, the rapid loss of energy is obviously of use where it is desired to damp out vibration. Hysteresis is measured by the area between the curve of extension and the curve of retraction.

Variations in the properties of natural rubber compounds are chiefly achieved by the use of various types of carbon black. The hard carbon blacks of extremely fine particle size increase the tensile strength—reinforce the rubber—but the resilience and " kick " of the rubber is decreased. Softer types of carbon black, of larger particle size, do not affect the resilience to the same degree, but on the other hand, do not give such high tensile strength—they are " semi-reinforcing " blacks. As a consequence it is necessary to vary the material to be added according to the requirements of the product. This behaviour is also shown by many synthetic elastics as will become clear in the ensuing discussion.

Plasticity of Synthetic Rubbers. The plasticity of synthetic rubbers is of paramount importance. It is this factor which dominates the present characteristic of the material. In manufacturing synthetic rubbers it is essential that a speedy method should be available for determining plasticity. The American method employs the Mooney plastometer. The German procedure is based on the plasticity which they call the Defo number.

Latterly, the Mooney plastometer has become one of the most favoured instruments for testing rubber, particularly synthetic rubbers.

Most specifications now refer to Mooney plasticities and it is widely employed in testing work. The instrument shows the torque required to turn a rotor at constant speed in a confined sample of the rubber under test maintained at constant temperature. Changes of plasticity with time, as the material becomes tougher or softer, result from a shearing action. This is parallel to the action occurring on a mixing mill or in an internal mixer. The reading after 4 minutes at some definite elevated temperature is generally taken as the measure of the viscosity.

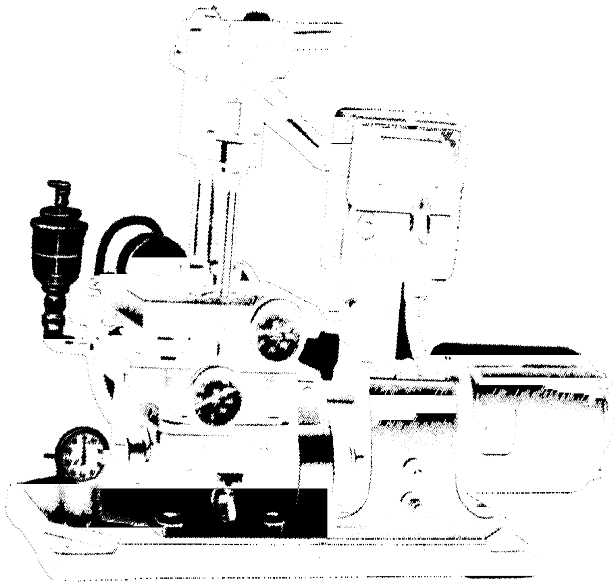


FIG 52—Mooney Plastometer

Mooney Plastometer. The instrument is rather complex, but the essential parts are shown in Fig. 52. The roughened surfaces between which the rubber is sheared consists of the disc-shaped rotor and the upper and lower halves of the stator. The two halves of the stator form together a closed cylindrical chamber, in which the rotor is vertically centred by means of a shoulder and by a pin in the centre of the chamber roof. The surfaces of both rotor and stator are ridged, and pressure on the rubber is maintained by a pair of plungers forced downwards by springs. The shaft of the rotor fits into the spindle and is slotted to receive the key in the spindle. This spindle carries the

worm gear which engages with the worm mounted on a horizontal shaft. The spur gear on the end of the shaft engages with a pinion on the shaft of a synchronous A.C. motor. The shaft is free to move longitudinally in its bearings, and to rotate, but its horizontal travel is opposed by a leaf spring supported in a clamp. The horizontal travel of the shaft, which is equal to the deflection of the spring, is indicated by a micrometer gauge. The upper and lower platens can be heated by steam or electricity, and the upper platen can be moved vertically by means of a double lever system operating through a connecting rod.

The dimensions of the rotor and stator are as follows:

	Diameter	Thickness	Depth
Rotor	3·810 cm.	0·544 cm.	—
Stator	5·080 cm.	—	—
Stator chamber	—	—	1·062 cm.

The speed of the rotor is two revolutions per minute, and the pressure exerted by the plungers is 30 to 60 kg./sq. cm. The temperature at which the measurements are determined is 100° C.

Operation. The rotor disc and stator are lightly brushed with soap solution to minimize the sticking of the rubber. A slab of rubber is then placed above and below the rotor, which is then placed in position and the plastometer closed. Excess rubber is forced out and resistance to this forced flow builds up a back pressure within the chamber forcing up the plunger. After the plastometer is closed the rubber is warmed up for one minute, then the rotor is started. As the rotor begins to turn in the rubber, the shearing action exerts an opposing torque on the rotor, which transmits a horizontal thrust to the shaft. This thrust results in a deflection of the spring, which is then registered on a gauge. The gauge reading goes through a maximum during the first 2 or 3 seconds, and then begins to fail. If appreciable quantities of air are enclosed in the rubber the gauge will firstly pass through a minimum, until the plungers compact the mass, then the reading rises asymptotically to a constant value. In either case the reading is substantially constant within one minute of the motor being switched on. This reading is proportional to the stiffness or viscosity of the rubber and is called its "shearing viscosity".

Advantages and Disadvantages. The major advantage is the speed of operation. If properly cut, two to six samples from one large batch can be measured simultaneously to give a single average reading.

In accuracy or sensitivity it compares favourably with the Williams plastometer. The main disadvantage is that it is a machine as well as an instrument, and is therefore subject to wear.

The Defo Number. The Defo number has been used for many years in Germany. It is the standard reference in all rubber practice there. The specimen is cut from a slab as a cylinder 10 mm. in diameter and 10 mm. high. It is compressed at 80° C. It is compressed to 4 mm. in 30 seconds. The force in grams required to carry this out is the figure which is called the Defo Hardness. It is assumed to record the plasticity of the material. A high reading means a very hard material. The material is softer as the figure drops. After a release period of 30 seconds the height of recovery in hundredths of a millimetre is the measure and expressed as a percentage of the original height. This gives a measure of the elasticity. In practice it is found that a Defo number of about 3,000 corresponds to the Mooney reading of 160.

After the heat softening treatment the material as used for tyres had a Defo Hardness of about 700, and this corresponds roughly to a Mooney reading of about 55.

REFERENCES

[1] Barron, *Modern Rubber Chemistry*, Hutchinson, London, 1947.

[2] Davis and Blake, *Chemistry and Technology of Rubber*, Reinhold, New York, 1937.

[3] Memmler, *The Science of Rubber*, Reinhold, New York, 1934.

[4] Wood, *Proc. Rubber Tech. Conf.*, 1938, p. 935.

CHAPTER II

COMPOUNDING OF SYNTHETIC RUBBERS

The Incorporation of Materials into Rubber. The entire set-up of the world-wide rubber industry is based on the experience of a century. There is an enormous amount of machinery in operation and a huge pool of skilled labour available. The whole pattern of large-scale use of synthetic rubber is based on the existing rubber industry. The exigencies of the war situation made it impossible for any slow, deliberate, gradual build-up of special plant and technique. Advantage had to be taken of all existing facilities. Rubber practice is the dominating theme behind all synthetic-rubber manufacture.

It is therefore imperative to have a clear idea of the basic principles of rubber technology. The following account is an endeavour to provide such a background as a preliminary to a more detailed consideration of the synthetic rubbers. It is a fact that with almost every synthetic rubber there have been departures from normal processing practice. These variations are dealt with as the specific synthetic rubbers are considered.

It is imperative to realize that the chemical and physical behaviour of rubber alone or with sulphur is comparatively unimportant. From the practical point of view, rubber is always associated with other materials. This applies equally well to most synthetic rubbers. Consequently it is the phenomena observed in these more complex compounds which are of primary importance.

It is only on rare occasions that one encounters pure rubber, or what is known as a *pure gum* material, meaning just rubber and sulphur. Rubber products invariably contain a number of other materials. The reasons for the incorporation of other materials are quite clear. They may improve the quality of the product, they may facilitate the processing during manufacture, or they may cheapen these articles.

These facts were fully realized by the pioneers of the rubber industry. In the early days of rubber manufacture, every type of available material was put into the rubber-sulphur mixture in order to study the effect on vulcanization. Many of them were found to have a favourable effect on vulcanization, such common products, for example, as lime, litharge, magnesia and zinc oxide being used. Not only did they seem to shorten the time necessary for vulcanizing the rubber, but the final product showed marked improvements in its

properties. Apart from these, many other materials gave the product a fine finish or some desirable consistency, although having no effect on the physical properties nor on the time of vulcanization. More than a century ago both Goodyear and Hancock were known to employ such things as earth, talc, magnesium oxide, chromes, white lead, litharge and vermilion, while the latter had a patent for using asphalt.

Development of Standard Ingredients. Almost every known material has at one time or another been incorporated into a rubber mixing in order to try to achieve one or more of the above effects. Inevitably, the passing of time has seen established on a firm footing a number of ingredients which have come to be regarded as standard and are widely used. Nevertheless, it is a fact that no sooner does a by-product become available in any industry than it is sought to apply it to rubber, but rarely with any marked success. As more experience is acquired, so standard production patterns begin to take shape for synthetic rubbers.

In point of quantity, filling materials undoubtedly take first place since they are invariably cheap. In most cases their use depends largely on the price of rubber. Clearly when rubber is dear there must be a trend towards using larger quantities of cheap filling materials. If rubber is cheap, then the price of filling materials becomes less important, considerations of quality taking on primary importance. It is important to remember that commercial considerations outweigh any others.

As the rubber industry has shaken down and consolidated itself, so the whole trend of incorporating materials into rubber has been directed at making things easier. Standard mixes have become tacitly associated with certain productions. It is well known that certain filling materials may be employed for definite purposes within certain limits. It is only when violent economic fluctuations upset ordinary calculations that it becomes necessary to deviate from these limits. A typical example is the virtual disappearance of natural rubber due to war conditions introducing the necessity for adding as much as possible of other materials. It must be realized that in compounding the main object all the time is to reduce costs without sacrificing quality. Unless new materials can effect this they stand little chance of success.

What are the Materials added to Rubber ? A piece of rubber is taken and masticated on the mixing mill. This is quite a lengthy and arduous task. What can be done to make it easier ? The addition of a small quantity of plasticizer or softener will achieve this and will also reduce the time necessary to bring the rubber to any desired degree

of softness or plasticity. Now if the masticated stock is intended to be calendered to anything like a smooth sheet, or extruded, there may be difficulties encountered during these processes. The material may be too rubbery and tough. For this reason it may be wiser to add some *reclaimed rubber* to the mixing. Physical properties of the finished product are conditioned by adding filling materials (generally referred to as fillers). And of course to make an attractive article, colouring matter or pigments are necessary. So far, so good, but now comes the question of vulcanization. Straightforward vulcanization with sulphur takes some time to carry out, which is a disadvantage. To hasten this process *accelerators* are mixed into the compound together with something to activate them. When this has been done, vulcanization may be expected to yield a satisfactory product in a short time.

But it is found in service that such a product may deteriorate badly in a comparatively short time; it ages rapidly. Therefore we have to put something in which will, at least, retard this tendency. This necessitates the incorporation of *antioxidants*.

In addition to all these widely used classes of materials there are others which may appear to be redundant, yet which perform useful functions in special circumstances. Among them are materials which retard accelerators, i.e. in effect put the brake on them. There are also stiffening materials acting in the reverse way to softeners. There is also the class of materials quite widely used for many purposes —*rubber substitutes*, as they are called.

Order of Adding Materials. In the preparation of compounded rubber for manufacture, experience over many years has established that the most satisfactory results are achieved by incorporating ingredients in a definite order. The order most generally recommended and used is:

1. Rubber.
2. Reclaimed rubber.
3. Peptizers.
4. Plasticizers and softeners.
5. Fillers.
6. Accelerators.
7. Antioxidants.
8. Sulphur.

In the case of many synthetic rubbers this order is no longer adhered to.

The master batch principle is widely used for ingredients such as sulphur, antioxidants, and some fillers. A master batch of sulphur

would consist of equal parts of rubber and sulphur mixed on a mill. The requisite small amount required to provide the necessary sulphur for any mixing would be added to the compound on the mixing mill.

Addition of Sulphur. Sulphur is the fundamental addition to rubber. It is equally fundamental for most synthetic rubbers, other than neoprene.

Masticated rubber is soft and plastic. Mixed with sulphur and heated, its physical properties change entirely. It gradually becomes increasingly elastic and tougher. The mechanical properties improve as the heating is continued until an optimum value is reached. If continued beyond this stage the physical properties decline, strength decreases and the rubber becomes shorter and shorter; if carried still further the rubber eventually becomes tacky and once again plastic, a process known as "reversion". The early stages of over-vulcanization tend to promote "blooming" of sulphur, i.e. finely divided sulphur appears on the surface.

As vulcanization proceeds the rubber combines with more and more sulphur (if available) and becomes progressively less affected by solvents. It is less swollen by these and will not disperse in them. This is in marked contrast to the behaviour of the masticated rubber. The resistance to solvents becomes more pronounced as the amount of sulphur combined with the rubber increases.

Vulcanization is also known as "curing" and the process is often referred to as the "cure".

After vulcanization not only have the physical properties altered but chemical changes are apparent too. A certain amount of sulphur appears to combine with the rubber and is referred to as "bound sulphur" or combined sulphur because it cannot be removed even by the most drastic chemical treatment. The amount of combined sulphur per 100 parts of pure rubber is known as the vulcanization coefficient. Sulphur which can be extracted easily from the vulcanized rubber is known as "free" sulphur.

The smallest known amount of sulphur, which, combined with rubber, shows incipient vulcanization, is 0·15 per cent., while the largest amount of sulphur which combines with rubber in the ordinary way, is 32 per cent. This is the proportion present in hard rubber or ebonite.

Combined sulphur cannot be removed from vulcanized rubber. Indeed, in chemical reactions to which the vulcanized rubber may be submitted the sulphur invariably accompanies the rubber in any changes. It seems certain that the sulphur tacks on at the double bonds of the rubber since the degree of unsaturation decreases.

At the present time the tendency is for the amount of sulphur used in vulcanized rubber to decrease. However, standard products are used where as much as 4 per cent. of sulphur is combined. But between 4 per cent. and 25 per cent. there is a hiatus. Rubbers containing such proportions of sulphur, known as semi-ebonite, are definitely inferior in tensile properties and other desirable properties, and are not commercially used to any appreciable extent. After this proportion of sulphur (25 per cent.) is reached, however, the rubber acquires the characteristics of ebonite, the product once again becoming commercially important. In the case of GR-S there is no hiatus between 4 per cent. and 25 per cent. combined sulphur.

Peptizers. A number of classes of chemicals have been found which will function as chemical plasticizing agents. These are referred to as peptizing agents.

Among the more important of these are the aromatic hydrazines such as phenyl-hydrazine; the thio-acids such as thio-benzoic acid; certain nitroso compounds such as nitroso-β-naphthol; and by far the most important class the aromatic mercaptans, such as β-naphthyl mercaptan.

In most cases the peptizers function as catalysts during the milling operation, the mill being run much hotter than usual, temperatures of the order of 100°–120° C. being used. Very small amounts of the order of 0·5 per cent. are adequate. There is great saving in power consumption and the time of milling when peptizers are used.

The same effect is found in processing GR-S and other synthetic rubbers. The materials employed have followed a similar pattern. All the above materials are effective in aiding the thermal softening of GR-S. Other materials used include benzaldehyde phenyl hydrazone, some furfural derivatives, and iron naphthenate.

Plasticizers and Softeners. Raw rubber is a very tough material, requiring intensive mechanical and heat treatment to soften it sufficiently for the incorporation of fillings. In order to render this process easier it has been customary to add various modifying materials to rubber at a very early stage of mastication. Suitable substances are vegetable and mineral oils, waxes, tars, pitches and resins. Some are solid, while others which are liquids tend to swell and soften the rubber, an effect which greatly assists plasticization. They perform a number of useful functions, which may be summarized as:—

1. They reduce the amount of mechanical work required to bring raw rubber to a soft and masticated condition.
2. They soften the rubber, thereby making easier the subsequent addition of filling materials.

3. Some have a profound effect in dispersing fillers throughout the rubber.
4. They allow mixing to be carried out at low temperatures which help to prevent "scorching" in the final stages.
5. They render mixes, containing high loadings of fillers, soft enough to be workable in subsequent processes, such as calendering and extruding.
6. Where tacky and adhesive properties are desirable they assist in conferring these.
7. Some of them have a profound effect in rendering rubber waterproof and gasproof.
8. In many cases there is a beneficial effect on the ageing properties of the rubber.

Softeners. Burbridge[4] divided softeners into two groups:

(*a*) True softeners, which actually dissolve in rubber; among these he included—mineral rubber, other bitumens and pine tar.

(*b*) The pseudo-softeners, which merely mix mechanically with the rubber, acting as lubricating agents. This type tends to separate after a time, blooming to the surface. Among them are paraffin wax, stearic acid and mineral paraffins.

He gave the order of softeners according to the effect on plasticity as: oleic acid, stearic acid, pine tar, ceresin, mineral rubber, rosin, naphthalene, mineral oil, rubber resin, palm oil, palmitic acid, rape oil, olive oil, petroleum jelly, linseed oil, rosin oil, carnauba wax.

Plasticizers and softeners for rubber do not function equally well with synthetic rubbers. Perhaps the best example is pine tar. This is most effective in rubber, but is relatively ineffective in GR-S and Buna-N rubbers. This difference of behaviour has been particularly evident in respect to the tackiness of the synthetic rubbers. Most synthetic rubbers are devoid of the inherent tackiness of natural rubber. This is a serious defect and tack producers are essential. Only moderate success has been attained with standard ingredients and many new materials have been developed. The specialized materials employed in these cases will be dealt with in subsequent chapters when the technology of the synthetic rubbers is considered individually.

Materials new to rubber technique include the standard plasticizers employed for paints and plasticizers; low molecular weight polymers and butadiene and styrene such as plasticater 32; materials such as the German Koresin; naphthenates, and so on.

Bitumens. These are popular softeners and fillers for rubber. They include so-called mineral rubbers, which comprise natural

products such as gilsonite, and also petroleum residues, asphalts, and so on. They are much less important in synthetic rubber compounding. The use of bitumen in rubber was put on a sound basis by Weber.[18] At the present time large quantities are used for tyres, flooring, cables, ebonite, footwear, and so on, while softer types are used in many mechanical articles. Weber showed that 7 per cent. in a mix gave very favourable properties, while up to 20 per cent. could be used without appreciably affecting mechanical properties. They are inherently suitable on account of their insulating properties. Their popularity is largely due to low cost and low specific gravities which enable them to be used as cheapeners.

Stearic Acid. The presence of stearic acid in raw rubber was established by Whitby.[19] He also studied the effects of its removal from and addition to rubber mixings. Poor grades of crude rubber are invariably deficient in their natural stearic acid content; thus the addition of stearic acid may in some cases change a poor crude rubber to one of first-class grade. Stearic acid also acts as a softener and assists in the dispersion of the various materials added during compounding. Quantities ranging from 1 to 5 per cent. are invariably used in rubber practice.

Oleic acid is equally effective in these functions, but has a marked tendency to "bloom" on the surface, spoiling the appearance of the product.

These materials do not have the same significance in synthetic rubbers.

Coumarone Resins. Coumarone resins derived from coal-tar are very effective plasticizers and softeners for rubber. They enhance the tackiness and processing properties. They are effective in synthetic rubbers and are widely used.

Extenders. Extenders have been defined as "materials which possess plastic or rubber-like properties so that they can be used to replace a portion of the rubber". In fact, they act as diluents. These materials are unsaturated hydrocarbons of the general formula $(C_3H_4)n$, derived from certain acid sludges formed in the refining of mineral oils. The characteristics of all types are somewhat similar. They have acquired some significance as compounding ingredients for synthetic rubber. They aid the processing and the tack. They have found very wide usage in German practice.

The American Naftolens are reddish-brown in colour, and have a green fluorescence. They are available in several grades with different viscosities ranging from solid to liquid.

Naftolen is capable of co-vulcanization with rubber, and in addition

it activates accelerators. It is also useful in so far as it acts as a dispersing agent for fillers, particularly carbon black.

Further outstanding properties are these:

(*a*) Increases age resistance to compounds containing carbon black and high proportion of sulphur;

(*b*) Retards sulphur "bloom";

(*c*) Imparts good surface tack, this of particular interest in type compounding;

(*d*) Good electrical properties, making it desirable for cable compounds and other electrical products.

The type best suited for this purpose is Naftolen 550.

Dielectric constant at 60 cycles and 20° C.	4·47
Power factor	0·077
Loss factor	0·228
Breakdown voltage	48 kv.

The material also finds application in latex and in the reclaiming process.

A number of materials somewhat similar to Naftolen are being marketed in this country under the trade names of "Iranolines" and "Ravolens", etc. These aromatic extract extenders are also available in various grades ranging from liquid to solid. They are high-boiling aromatic extracts and find extensive use in rubber, synthetic rubber, and rubber-like plastics.

Rubber Substitutes. Rubber substitutes or *factices* form a class of materials which is widely employed in rubber compounding. They are groups of materials obtained from vegetable oils, usually by combination with sulphur. Being very rubber-like in appearance and possessing slight elasticity, the derivation of the name is easy to trace. Substitutes mix into rubber without difficulty. They form homogeneous materials which can take up more mineral fillers than the rubber alone. Addition of substitute undoubtedly detracts from the strength and other physical properties of rubber, and regarded on this basis it is merely a diluent.

At one time the use of factice depended on its low price in relation to rubber. Although for many years regarded merely as economic substitutes for rubber, their intrinsic properties soon associated them inseparably with certain manufactures, owing to the ease of production. At the present time their use depends on the particular properties conferred upon the finished product.

The chief types of factices are the heat-cured brown substitute and the cold-cured white substitute. The latter type is thought to have been first produced by Parkes.[15] However, both became available to

the industry about the same time, 1846. Brown substitute is made by heating rape oil, linseed oil, or cotton-seed oil, with sulphur. The white substitute is produced by employing sulphur chloride instead of sulphur. Other types are produced by combined treatment with sulphur and sulphur chloride. The production is, in effect, vulcanization of the oils, analogous to sulphur vulcanization and cold-cure of rubber, respectively.

White substitutes are chiefly used for those materials which are themselves to be cold-cured with sulphur chloride, such as single-texture proofings and thin calendered sheet. According to Lloyd [12] it confers flexibility, exceptionally silky finish and good ageing properties. The article which generally contains most white substitute is the eraser, which may have as much as three parts to one part of rubber. In heat-cured articles, white substitute tends to retard the acceleration owing to development of acidity. To some extent this is offset by adding fillers such as lime and magnesia. ✓

Brown substitutes are employed mostly for heat-cured products. Among them may be mentioned tubing and packing strips, soft hose linings, soft rollers, sponges and double-texture proofings. They confer very smooth-working properties on mixes which are to be extruded.

These rubber substitutes find particular use in neoprene compounds.

Dependence of Rubber Properties on Fillers. The physical properties of rubber products depend to a great extent upon the nature and quantity of the fillers that have been added. It is these physical properties which primarily determine the utility of any rubber article in use. The following list of these properties gives some idea of the complexity of the system:

Tensile strength; modulus; hardness; elongation; specific gravity; tearing properties; resistance to abrasion and flexing; permanent set; inflammability; thermal conductivity; electrical properties; resistance to moisture, solvents, and chemicals; ageing; odour and taste; and so on.

The relative importance of these properties depends almost entirely upon the use to which the product is to be put. Behaviour of the vulcanized material containing fillers is compared with the same mixing from which the filler is omitted. Not many filling materials exert any positive effect on the more important physical properties.

The Change in the Use of Filling Materials. Until 1918 a tyre tread contained a large variety of materials such as whiting, magnesium carbonate and lead compounds. Many of these were employed merely to increase the volume of the material and to cheapen it. In the tread of 1912 the small amount of lamp black contained was used to give a

grey tyre, but in 1918 the amount of black employed was far above any possible requirement for pigmentation alone. At the same time the amount of zinc oxide had gone down. In the present-day rubber treads, carbon black has gone right up, zinc oxide is very low, while other filling materials have almost disappeared. Evidently the use of this black has some other significance than mere colouring of the rubber. Actually it has been found to have a remarkable influence on the physical properties of the product. It makes the rubber stiffer, tougher, harder, more difficult to tear, stronger and more resistant to abrasion. This is the so-called reinforcing effect of filling materials. The carbon black is superior to zinc oxide, which in turn is superior to all the others.

Fillers in general are considered in two main groups:

(*a*) Those which have a pronounced effect on the tensile strength, increasing this and also enhancing resistance to abrasion, to tearing, and to flexing. These are called reinforcing fillers and include first and foremost carbon black, other blacks such as lamp black and acetylene black, zinc oxide, magnesium carbonate and china clay.

(*b*) Filling materials which seem to have no influence on these properties, but nevertheless perform a number of useful functions. For example, they may confer on a rubber compound easier processing properties, they may give rigidity or hardness, resistance to chemical attack, and, perhaps most important of all, they reduce the cost. These, known as the "inert" fillers, include whiting, barytes, blanc-fixe, lithopone, talc, kieselguhr, slate dust, and many others.

The desirable features which all fillers should possess in common, are fine and regular particle size, absence of gritty particles, and the absence of moisture. The latter feature is particularly undesirable since it inevitably causes the vulcanized product to have blisters and to blow. At one time it was customary to add a little lime to take up any moisture, but nowadays preliminary drying is found more satisfactory.

In connection with the incorporation of filling materials into rubber it is interesting to notice that the important factor is not the weight of the filler, but its volume. This arises from the fact that volume cost, not weight, determined the ultimate cost of rubber products. Consequently the specific gravity of fillers is their important property. Heavy fillers are at a disadvantage. Among these may be mentioned zinc oxide 5·6, litharge 9·3, vermilion 8·1. At the other end of the scale are carbon black 1·8, magnesium carbonate 2·2, and kieselguhr 2·2.

Barytes or Barium Sulphate. Barium sulphate occurs naturally in the form of heavy spar, which is ground to a fine powder for use as a rubber filler. It has a high specific gravity of about 4·5, and if used

to any large extent will give a very heavy product. There is a specially prepared material which is superior to the natural product. This is known as blanc-fixe and is prepared by treating barium salts with sulphuric acid. It is obtained as an almost white powder. Extensively used in rubber manufacture, it is extremely inert and resistant to all forms of acid. Consequently rubber products which have to come into contact with acid are generally filled with barytes. In quite large proportions it does not unduly decrease the resistance and elasticity of rubber.

Whiting. The most widely used filler in rubber compounding is whiting. This is calcium carbonate, obtained either by grinding limestone or as a by-product in the chemical industry. In the latter case it is obtained when sodium hydroxide is produced from lime and sodium carbonate. Owing to its relatively low specific gravity, 2·7, and its cheapness, it has found very wide use. It has a number of disadvantages. The particle size varies considerably, and the material disperses badly in mixing. Some of the physical properties of rubber are unfavourably affected by its use. Although inert in all other respects, it cannot be used in compounds which are likely to come into contact with acids, since it will decompose.

In recent years a trend has developed for treating inert fillers, particularly precipitated whiting, to improve the properties. One method has been to subject the particles to the action of fatty acid, which causes them to become coated with the calcium soap. There are several such materials available, many of them coated with stearic acid. It is claimed that they mix more easily and disperse better, give superior tensile properties and confer general improvement in physical properties.

Silene EF is hydrated calcium silicate of very fine particle size. It imparts excellent tear and abrasion resistance. It is a highly effective white reinforcing filler in GR-S.

Other Inert Fillers. Kieselguhr is a comparatively light white filler (specific gravity 1·6 to 2·0) which is becoming increasingly popular. It is the finely divided silica remains of diatoms and other organisms. It has low heat conductivity and is inert to heat, steam, and chemical attack. Talc or "french chalk" is another filling material, used extensively as a dusting agent, on account of its fine particle size and greasy feel. Talc is found to be a satisfactory material for embedding articles during steam vulcanization. It is a hydrated magnesium silicate.

Silica is an inert filler in rubber. However, new forms have been developed which are very effective reinforcing agents, particularly in

GR-S. They have been referred to as "white carbon black"! The Germans claim to have developed a form of silica by precipitation from silicon tetrachloride which they claimed was almost as effective as carbon black in Buna S. Similar types have been evolved in the United States.

The Germans also developed a special aluminium hydrate known as "tonerde gel". As a white filler it gave fair tensile strength to Buna S, but only moderate resilience.

Lithopone is a popular white pigment and filler, having exceedingly fine particles, stated to be 0·3 μ in diameter (Green).[10] It is formed by the reaction between barium sulphide and zinc sulphate and is a complex of barium sulphate and zinc sulphide.

$$BaS + ZnSO_4 \rightarrow ZnS + BaSO_4$$

TABLE 75. CHANGE IN TYRE TREAD COMPOSITIONS OVER A PERIOD OF YEARS[14]

Materials	1905	1912	1918	1940
Rubber	50	50	90·3	100
Reclaimed rubber	100	100	19·4	
Zinc oxide	30	89	40	5
Sulphur	20	3·75	6·3	3
Whiting	20			
Magnesium carbonate	—	3·5		
Lamp black	—	0·3		
White lead	29			
Blue lead	—	—	0	
Lime	6	1·25		
Aniline	—	2·5		
Hexamethylene-tetramine	—	—	1	
2-Mercaptobenzothiazole	—	—	—	1·25
Pine tar	—	—	—	4
Asphalt	—	—	15·5	
Fatty acid	—	—	—	3
Phenyl-beta-naphthylamine	—	—	—	1
Carbon black	—	—	12·4	50
Litharge	30			

PHYSICAL PROPERTIES OF TREAD STOCKS

	1905	1912	1918	1940
Time of vulcanization in minutes at 275° F.	60	60	60	30
Load to cause 400 per cent. stretch (lb./sq. in.)	—	725	900	1925
Tensile strength (lb./sq. in.)	1100	1600	3150	4225
Tensile after artificial ageing with oxygen at 300 lb./sq. in. pressure at 158° F.	575	650	1425	3550
Per cent. decrease in tensile strength after artificial ageing	48	59	55	16

Reinforcing Fillers. The addition of suitable amounts of certain compounding ingredients were found to increase enormously the wear-resisting powers of rubber. The properties thus conferred were largely expressed by the shape of the stress-strain curve obtained by testing the vulcanized products. A base mix was selected and regularly spaced increments by volume of the more important compounding ingredients added. It was at once seen that profound changes in the character of the stress-strain curves were obtained. They could be divided into two distinct classes.

By addition of barytes a curve was obtained which was similar to that of the base mix, except that the breaking-point occurred earlier. Such a pigment merely diluted the mix, and had little effect upon the mechanical properties. They are merely diluent fillers.

The other type of ingredient had a profound effect on mechanical properties. If carbon black or zinc oxide were added to a rubber mix, there was much improvement. The curvature of the stress-strain diagrams tended to disappear. Rubber could be compounded to display almost the same behaviour as steel. These fillers are invariably incorporated into rubber products which have to stand up to exacting mechanical conditions.

Magnesium Carbonate. This is a white filler of which there are two types available. Light magnesium carbonate is composed of magnesium carbonate combined with hydrated magnesia. It is considerably less dense, with a specific gravity of 2·2, than heavy magnesium carbonate, which is the pure carbonate, specific gravity 3·1. The latter is prepared by grinding the mineral magnesite.

Magnesium carbonate is extensively employed in rubber compounding both to reinforce and to stiffen materials. Up to about a loading of ten volumes it is superior to any filler for reinforcement. The excessive permanent set is a disadvantage. It has a deadening effect on rubber, which is made use of in the production of articles such as soles and flooring. This effect is partly due to the considerable set which occurs when rubber containing it is stretched, thought to be due to orientation of the needle-shaped particles of the filler.

Magnesium carbonate has a refractive index (1·53) which is so near to that of rubber that its pigmenting value is very low. Because of this it is used in making transparent rubber.

China Clay or Kaolin. A range of clays are very popular as filling materials for rubber. Outstanding characteristics are the low cost, the reinforcing effect and the stiffening effect. Among them are hard clays which have a pronounced stiffening and hardening effect, and soft clays which are not so effective. There are numerous pro-

prietary types of materials in this class. The latter type are employed where heavy loadings are wanted without too much stiffening. They are inferior to the hard clays from the point of view of reinforcement and abrasion resistance; 166,000 tons of kaolin were used in 1947 in U.S.A.

Chemically they are hydrated magnesium silicates, which are very stable towards chemical attack and are used extensively for this reason. The one great disadvantage of clays is that they have a bad effect on the resistance of rubber to tearing.

Zinc Oxide. Until about 1920 the most important filling material was undoubtedly zinc oxide. Not only did this filler give a fine white product, which vulcanized smoothly without trouble, but it improved the strength and other properties of rubber in a profound and unmistakable manner. Since the advent of carbon black, zinc oxide has lost its importance as a filler. For it has some disadvantages. The chief is its high specific gravity, 5·6, which makes it an expensive filler to use. Consequently reinforcement in light-coloured mixes is more cheaply obtained with china clay or magnesium carbonate, while for dark mixes there is the superior carbon black. However, what it has lost in reputation as a filler, has been more than made up by the recognized importance of zinc oxide for other purposes. It is the most important activator of vulcanization. For this reason it is used in almost every rubber mixing, latex mixings included. It seems to stimulate accelerators into action, for they do not function without it.

Zinc oxide is used in every type of vulcanizable synthetic rubber as a promoter of vulcanization. In the case of neoprene it acts as the accelerator. The U.S. used 82,000 tons of zinc oxide in 1947.

To a large extent it owes its exceptional pigment properties to the fine particle size, now reduced to as low as 0·15 μ. It is obtained in a number of grades, classified according to the lead content. The presence of even minute quantities of this metal causes the final product to darken slightly—an obvious disadvantage where light colours are wanted.

Zinc oxide alone is insoluble in rubber and as such is ineffective as an activator for accelerators; the presence of stearic acid enables it to form rubber-soluble zinc stearate, when the action works smoothly.

Carbon Black. As has already been foreshadowed, the most important filling materials employed in rubber manufacture are those coming within the description of carbon black. Their importance becomes evident when it is realized that in 1947 no less than 1318 million lbs. were used annually in rubber. There are a number of types, made in different ways, possessing rather different properties, and accordingly used for different purposes. The important feature

is the particle size. In synthetic rubbers such as GR-S the important feature is the method of production. Furnace black, which is much softer than channel black, is the predominant type.

It is now accepted that the first practical use of carbon as a filler in rubber was at Silvertown by Mote in 1906. The absence of accelerators, however, prevented full realization of its properties. The early use of carbon black in tyre treads has been attributed to Oenslager,[13] of accelerator fame. The proportion, at first sufficient to act merely as a pigment, increased until 1925, when a volume proportion of about 25 per cent. became standard for tyre-tread production.

Parkinson[16] has outlined the manner in which properties are affected by carbon black particle size. The properties which depend more on fineness of division than on other factors are rebound resilience, abrasion resistance, tensile strength and tear resistance. The lower limit of particle diameter for best tensile strength and tear resistance appears to be higher than that for abrasion resistance. Hardness and electrical conductivity are properties which depend at least as much on other factors as on particle size. Stiffness (modulus) depends more on other factors than on particle size. Factors modifying the effects of particle size (or specific surface) include the presence of carbon-carbon structures and a reduction in strength of bond in rubber-carbon structures. He considers that carbon black exists in rubber in four states : agglomerated, flocculated, dispersed, and bonded to the rubber molecules (the reinforcing fraction).

There is considerable confusion regarding the nomenclature. This has become worse owing to profound changes which have come about due to war conditions. Newer types have come into great prominence, particularly to ease the processing of synthetic rubbers. There are the following main divisions :

1. *Channel black or Gas Black.* This is regarded as the outstanding filler from the point of view of improving rubber properties. It is the finest (i.e. smallest particle size) black available. It is made by incomplete combustion of natural gas. The flames of burning gas impinge on metal surfaces and the black deposits. For this reason these blacks are also referred to as the impingement channel blacks. Owing to their extreme fineness the size of the particles has not yet been satisfactorily determined. While Green[10] considered the average diameter as 0·15 μ ($\mu = \frac{1}{1000}$ millimetre), Grenquist[11] placed the diameter in the range between 15 mμ to 200 mμ (1 m$\mu = \frac{1}{1,000,000}$ millimetre). The finest size now is known to be 13 mμ.

According to Cranor[5] the particle sizes of commercial grades which enjoy large use in industry range from an average diameter in the

neighbourhood of 30 mμ all the way down to 13 mμ. Surface area provides an even better point of view for consideration of the rubber grades which range from 10 to 12 acres per lb. Specialty grades used for ink and paint range up to 22 acres; the latter figure corresponds to the particle diameter of 13 mμ.

There are three main groups of impingement channel black accounting for practically all material of the channel category used in rubber. These are: (1) the fine extra reinforcing, (2) the standard reinforcing, and (3) the coarse or easy processing type.

These can be distinguished on the basis of available surface area, considering the extra reinforcing type as a "fine channel" black, since it has a surface area in the neighbourhood of 11½ acres per lb. The standard reinforcing type might then be classed as "medium channel" black, based on its surface area of from 10½ to 10¾ acres per lb. Material of clearly coarser particle size, for example, such as possesses a surface area of not more than 10·3 acres per lb., could properly be distinguished for the other grades by the designation "coarse channel" black.

2. *Acetylene-black.* This is produced by the explosive combustion of purified acetylene in closed chambers. Comparatively little work has been carried out to determine its particle size, which is thought to range between channel black and lamp black.

3. *Lamp-black.* This is obtained by incomplete combustion of fats, oils, tars, etc. Its particle size according to Green (*loc. cit.*) is mainly between 0·3 μ and 0·4 μ, and goes up as high as 1 μ.

TABLE 76

Carbon	Mean diameter (mμ)	Acres per lb.	Specific surface (sq. cm. × 10^4 per gram)
Thermatomic black	274	1 acre	10
Lamp black	97		23
SRF furnace black (Gastex, Furnex)	82–83	3·5–4 acres	31
Fine thermal black (P-33)	74	4 acres	36·5
Acetylene black (Shawinigan)	43		65
Kosmos (Dixie)-40 black	41		63
Statex black	34		75
Coarse impingement black (Spheron-9)	30	10·3 acres	86
Medium impingement black (Standard Micronex, Kosmobile-HM and Spheron-4)	28	10·5–10·75	94·5
Fine impingement black (Spheron-1)	24	11·5–12	107
Fine colour black (Super-Spectra)	13		198

TABLE 77. CHANNEL BLACKS

Group	Brand names	Producer	Characteristics and properties
EPC **Easy Processing Channel**	Spheron *No. 9* Micronex *W-6* Continental *AA* Wyex Kosmobile 77 Dixiedensed 77 Witco *No. 12*	Cabot Columbian (B & S) Continental Huber United United Wishnick-Tumpeer	Larger particle size, smaller surface area, easy processing, more resilience, lower heat build-up, good tear and abrasion resistance *Use* Synthetic and natural rubber tyre treads, industrial solids, wire jacket, etc.
MPC **Medium Processing Channel**	Spheron *No. 6* Standard Micronex Continental *A* *TX* Kosmobile (*S-66*) Dixiedensed (*HM*) Witco *No. 1*	Cabot Columbian (B & S) Continental Huber United United Wishnick-Tumpeer	Standard rubber black, medium particle size, normal processing, good tear and abrasion resistance *Use* Synthetic and natural rubber tyre treads, tank track blocks, wire jacket, conveyor belting, moulded goods
HPC **Hard Processing Channel**	Spheron *No. 4* Micronex *Mark II* Continental *D* *HX* Dixiedensed Kosmobile *S* Witco *No. 6*	Cabot Columbian (B & S) Continental Huber United United Wishnick-Tumpeer	Finer particle size, larger surface area, harder processing, excellent tear and abrasion resistance *Use* Tyre treads, soles, heels, conveyor belting, mechanicals
CC **Conductive Channel**	Spheron *I* Spheron *C* Spheron *N* *R-20* *R-30* *R-40* *CX* Voltex Conductex	Cabot Cabot Cabot Continental Continental Continental Huber United Columbian (B & S)	Very fine particle size, high surface area, imparts electrical conductivity, harder processing, excellent tear and abrasion resistance *Use* Tyre treads, soles, heels, conveyor belting, mechanicals where static dissipation and electrical conductivity are required

TABLE 78. FURNACE BLACKS

Group	Brand names	Producer	Characteristics and properties
SRF Semi-Reinforcing Furnace	Sterling *S* (pelletized) Sterling *R* (unpelletized) Furnex Continex Gastex & Pelletex Essex Kosmos *20* Dixie *20*	Cabot Cabot Columbian (B & S) Continental General Atlas Huber United United	Coarse particle size, high resilience, high loading capacity *Use* Footwear, synthetic tyre carcasses, inner tubes, hose, mechanical goods, moulded goods, insulated wire, automotive mountings, fuel cells, etc.
HMF High Modulus Furnace	Sterling *L* Statex *93* Modulex Philblack Kosmos *40*	Cabot Columbian (B & S) Huber Phillips United	Particle size finer than SRF, larger surface area, high resilience, low heat build-up good flex cracking resistance in synthetic rubber, high modulus *Use* Treads of heavy service synthetic tyres. Sidewalls of synthetic passenger tyres. Bogie wheels. Mechanical goods
FF Fine Furnace	Statex *B*	Columbian (B & S)	Fine particle size furnace black, high resilience, high loading capacity *Use* Footwear, synthetic tyre carcasses, tubes, hose, mechanical goods
CF Conductive Furnace	Sterling *I* Statex *A* *FB 200*	Cabot Columbian (B & S) Huber	Fine particle size furnace black, imparts electrical conductivity, high resilience, low heat build-up, high loading capacity *Use* Any furnace black stock where electrical conductivity is needed. When blended improves processing of conductive channel blacks
HEF High Elongation Furnace	Sterling *K*	Cabot	High elongation, high tensile, good thermal shortening properties, good cut growth resistance *Use* Footwear, synthetic tyre treads, tyre carcasses, tubes, hose, mechanical goods

TABLE 79. THERMAL BLACKS

Group	Brand names	Producer	Characteristics and properties
MT Medium Thermal	Shell Carbon Thermax Velvetex	Shell Thermatomic Columbian	Coarse particle size, low modulus, high resilience, very high loading capacity *Use* Mechanicals, moulded goods, automotive goods
FT Fine Thermal	*P-33*	Thermatomic	Finer particle size, low modulus, high resilience, high loading capacity *Use* Inner tubes, mechanical goods, moulded goods
Acetylene- black*		Shawinigan	Imparts electrical conductivity, high modulus, has high thermal conductivity *Use* In stocks where electrical conductivity is required

* This product is listed here because it is by process a thermal decomposition black. It is quite unlike other thermal blacks in rubber characteristics and it has *in part* the properties of HMF blacks, CF blacks, and CC blacks.

4. *Thermal or Thermatomic-black.* Thermal decomposition, or cracking of natural gas in the absence of air, yields thermatomic black. There is direct cleavage of the hydrocarbon molecule. It is said to be up to 274 mμ in particle size. These blacks have often been referred to as " soft blacks " owing to the ease with which they process. One pound of material has a surface area of 1 acre. It has been suggested that these should be referred to as " coarse thermal carbon ".

5. *Fine thermal furnace black.* Modification of this process involving gas dilution produces a much finer black (P-33), with particle diameter of 74 mμ. Characterized by tensile strength and tear resistance in natural rubber approaching the reinforcing blacks, but differing sharply by developing low modulus compounds, this type is sometimes referred to as " low modulus black ". " Fine thermal black ", however, affords a better description.

6. *Furnace black or Semi-reinforcing black.* It has been found that synthetic rubbers, notably GR-S, behaved better with the class of

blacks known as " furnace blacks ". According to Cranor as far back as the early '20's, gas carbon black was produced in a furnace by combustion of natural gas with controlled access of air. This procedure differs essentially from the method used to make channel black because the latter involves a *thermal surface action* to crack the hydrocarbon molecule. By contrast the furnace process employed to produce semi-reinforcing carbons depend on *flame*. The combustion furnace method differs radically from the channel method in that, on account of the size of the flame, collection by means other than impingement is necessary.

A typical carbon of this group is Furnex. The particle diameter of 83 mμ is only very slightly coarser than the 74 mμ diameter of P-33, and the surface area of this group averages in the neighbourhood of 4 acres per lb. This type is outstanding because it combines important reinforcing effect with high resilience. This type of material is known as *semi-reinforcing black*. It is a good practice to refer to this type by the convenient abbreviation " S.R. Carbon ".

The Germans produced their own range of carbon blacks mainly derived from coal-tar products. They burned naphthalene, phenanphrene, and anthracene oils by an impingement process. There was also a considerable production of acetylene black at Hüls as a by-product of the electric arc production of acetylene from marsh gas.

What are the Effects of Incorporating these Materials into Rubber ? When gas black, generally referred to by the family name of carbon black, is added to a rubber mixing which is vulcanized to optimum tensile values, a number of remarkable effects become apparent. When a sample is stretched it is much stiffer than with samples containing other fillers, i.e. it has a higher modulus. It is exceedingly strong and the force required to rupture a sample is very high, while the final extension decreases with increasing properties of filler. Other physical properties such as resistance to abrasion and resistance to tearing also improve, while ageing properties are enhanced. As the proportion of channel black is increased it is found that these properties also improve until a certain value is reached (about 25 per cent. by volume of the rubber), after which the properties decline. In general a somewhat similar effect is produced in synthetic rubbers.

Incorporation of channel black is a matter of some difficulty. The material, possibly owing to its fineness, is extremely reluctant to mix properly. It tends to form aggregates or clumps which are difficult to disperse. A great deal of heat is developed. In general it is desirable to prepare a master batch containing a high proportion of carbon black and add this to the necessary amount of rubber. The trend

is for internal mixers to be employed for carbon-black work. It is essential to employ stearic acid in the mixing in order for carbon black to function effectively.

Incorporation of suitable blacks in synthetic rubbers is easier than in the case of natural rubber. This is due to the fact that synthetic rubbers do not require the preliminary mechanical breakdown, hence fillers can be added very rapidly.

Carbon black has profound effect on properties other than the tensile strength of products. According to Wiegand,[20] the use of carbon black may be divided into three sections.

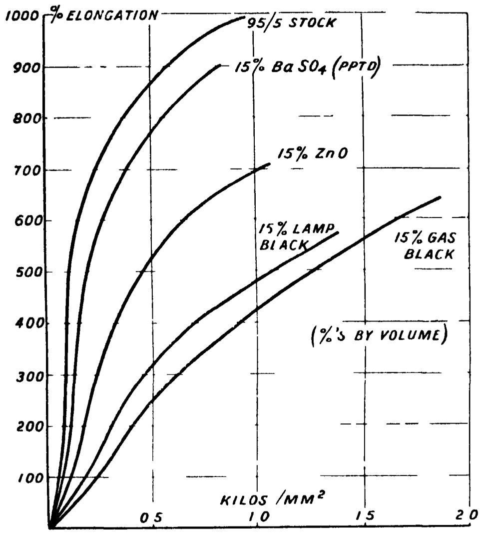


FIG. 53.—Effect of Filling Materials on Tensile Properties of Natural Rubbers

Up to the content of approximately 12·5 volumes (24 per cent. by weight), the tensile strength and energy absorption increase rapidly. After about 10 per cent., however, the electrical properties deteriorate very rapidly, particularly the resistivity and the breakdown voltage. Outstanding characteristics of such products are toughness and liveliness.

The second region extends up to 35-volume loadings, and includes products showing the maximum tensile strength, maximum resistance to abrasion and tearing, and highest energy absorption at 26·3 volume loadings (51 per cent. by weight). This section contains the majority of rubber products made at the present time, including tyre treads, conveyor belts, footwear, etc. Higher loadings than these result in products which still have good tensile strength and exceptionally high modulus and stiffness, but lacking in elasticity and flexibility.

While gas black confers remarkable strength on vulcanized rubber combined with many other desirable properties, yet there are cases where properties such as hardness and deadness are not desirable. It is also a matter of some difficulty to incorporate very large loadings. To overcome these difficulties softer types of carbon black, notably thermatomic carbon, are employed. Not being so bulky as carbon

black, they are more convenient to add to the rubber and mix without difficulty. It is claimed that up to three times the amount of rubber may be added. While stiffening and strengthening the rubber, yet there remains a desirable flexibility and extensibility which is lacking in comparable gas black mixes. Although reinforcement is not so pronounced as with carbon black it is nevertheless superior to other fillers; since it is low in price it finds extensive use for mechanicals, soles and heels, cables, and so on. In these cases it confers strength on the vulcanized product without the accompanying disadvantage of

TABLE 80. SPECIFIC VOLUME OF FILLERS

	Specific gravity	Specific volume (no. of c.cs. occupied by 1 gram)
Rubber	0·93	1·087
Carbon black	1·8	0·555
Zinc oxide	5·6	0·179
Whiting	2·7	0·370
Clay	2·6	0·385
Lithopone	4·1	0·246

TABLE 81. THERMAL CONDUCTIVITY OF RUBBER COMPOUNDING INGREDIENTS

Ingredient	Thermal conductivity cal. cm./cm.^{2} ° C. sec.
Zinc oxide, fast curing	0·00167
Iron oxide	0·00132
Dixie clay	0·00106
Lithopone	0·00092
Blanc-fixe	0·00078
Whiting	0·00084
Talc	0·00090
Magnesium carbonate	0·00057
Carbon black, slow curing	0·00066
Carbon black, fast curing	0·00068
Lamp black	0·00140
Graphite Acheson	0·00217

bad tearing, obtained with clay and magnesium carbonate. It is claimed that the ageing properties are superior to those of gas black.

One of the great snags about using gas black is the intense frictional heat developed during extension and retraction. Since rubber and gas black are both poor heat conductors, repeated stressing causes internal heat to be developed (in such articles as tyres). In cases where such effects become too serious, as in solid tyres, it is undesirable to use gas black, and lamp black is substituted. Although this does not give equal tensile strength and abrasion resistance, it is a much better heat conductor (see Table 81). This effect is illustrated by the

TABLE 82. COMPARATIVE EFFECTS OF FILLERS ON PHYSICAL PROPERTIES.

Filler	Optimum cure (min. at 40 lb.)	Modulus at 400 % (lb. per sq. in.)	Tensile (lb. per sq. in.)	Elongation at break (per cent.)	Hardness (shore)	Tear resistance (lb. per in. thickness)	Abrasion loss (c.c. in 10 min. × 100)	Impact resilience (% energy recovered)
Pure Gum Carbon-black :	20	435	3930	770	39	204	844	79
11·5 vols (21 lb.)	30	1250	4430	695	52	380	415	62
23 ,, (42 ,,)	30	2235	4895	640	68	655	292	42
46 ,, (84 ,,)	30	3670	3800	425	86	810	267	27
P-33 (a softer black) :								
11·5 vols. (21 lb.)	10	650	4150	720	45	355	528	76
23 ,, (42 ,,)	10	905	4140	690	50	400	570	69
46 ,, (84 ,,)	10	1385	3040	615	63	420	602	52
Zinc Oxide (fine particle) :								
11·5 vols. (65 lb.)	10	1050	3900	650	48	327	345	76
23 ,, (130 ,,)	10	1360	4015	660	57	420	482	71
46 ,, (260 ,,)	10	1850	3155	600	76	450	518	50
Dixie Clay :								
11·5 vols. (30 lb.)	20	1050	3845	680	48	80	640	74
23 ,, (60 ,,)	20	1740	3415	560	54	110	730	68
46 ,, (120 ,,)	20	2645	2645	400	65	148	870	55
Magnesium Carbonate (light) :								
11·5 vols. (25·5 lb.)	5	965	3835	665	49	90	550	73
23 ,, (51 ,,)	5	1315	3120	585	57	110	795	70
46 ,, (102 ,,)	5	2365	2365	400	67	168	806	55
Lithopone :								
11·5 vols. (48 lb.)	20	785	3930	705	47	125	605	76
23 ,, (96 ,,)	20	1190	3555	635	53	155	620	73
46 ,, (192 ,,)	20	1485	2810	565	63	260	788	66

Blanc-Fixe :								
11·5 vols. (48·5 lb.)	20	640	3485	685	46	125	570	75
23 ,, (97 ,,)	20	1050	3190	640	52	150	640	71
46 ,, (194 ,,)	20	1460	2235	510	64	220	887	65
Barytes :								
11·5 vols. (51 lb.)	20	455	3425	730	45	120	944	76
23 ,, (102 ,,)	20	560	2840	700	51	110	1160	74
46 ,, (204 ,,)	20	690	1995	615	61	95	1480	67
Whiting (Gilders) :								
11·5 vols. (31·5 lb.)	20	580	3360	710	45	60	843	78
23 ,, (63 ,,)	20	685	2875	675	51	63	1000	74
46 ,, (126 ,,)	20	800	1950	620	61	89	1365	68
Pyrax (a talc) :								
11·5 vols. (30 lb.)	20	505	3030	710	48	68	1024	77
23 ,, (60 ,,)	20	560	2480	675	55	76	1231	72
46 ,, (120 ,,)	20	645	1575	595	65	105	1225	66
Mineral Rubber :								
11·5 vols. (12 lb.)	20	430	3620	740	38	218	728	71
23 ,, (24 ,,)	20	435	3385	755	40	225	762	68
46 ,, (48 ,,)	20	420	2770	755	43	230	1162	59
Glue :								
11·5 vols. (14·5 lb.)	20	605	3755	740	38	75	624	74
23 ,, (29 ,,)	20	880	3470	680	41	62	703	73
46 ,, (58 ,,)	20	1345	3015	595	44	58	956	69

Pure gum base was:

Rubber	100	
Stearic acid	1	
Antioxidant	1	
Zinc oxide	5	
Sulphur.	2·75	
Altax	1	(Benzthiazyl disulphide)
Tuads	0·1	(Tetramethylthiuram disulphide)

fact that the tread of tyres used on racing cars is only $\frac{1}{8}$ inch thick. A thicker one would fail owing to the heat developed.

Inorganic Colouring Materials. The qualities necessary in materials intended for colouring rubber are good tinting power, hiding power, fastness to light, resistance to hot vulcanization and low cost. Initially, most inorganic pigments were borrowed from the paint industry and adapted to rubber practice.

White. Although one of the most popular shades, this is one of the most difficult effects to produce with rubber, there always being a tendency for the final product to darken. Latterly, with the use of fast accelerators enabling faster cures at lower temperatures, satisfactory white, in common with other colours, is being attained.

Lithopone, zinc oxide, and titanium dioxide are the principal fillers used to give white products. The latter is the best white filler available, and is said to have five times the whitening power of any other. The particles have very fine particle size and exceptionally good covering power, being better than zinc oxide or white lead. Having found wide application in the paint industry for this reason, it has proved equally successful with rubber. A mixture of titanium dioxide and barium sulphide known as titanium white gives very much better white pigmentation than might be expected from the composition. Other whites such as barytes, whiting and magnesium carbonate exert little tinting effect on rubber.

Red. Inorganic materials giving different shades of red colour are vermilion, iron oxide, and antimony sulphides.

Vermilion. This is a very heavy filler, specific gravity 8·1, and relatively expensive. Exceptionally good red colours are obtained with it, and it is still in good demand. Non-toxic, it is particularly used in the production of hard rubber dental plates, giving a satisfactory natural colour. Although there are natural deposits, nearly all is made by distilling mercury and sulphur.

Iron Oxide. Red oxide, or turkey red, is a popular and cheap red filler. Obtained by calcining iron sulphate, it gives a satisfactory, if rather dull, red colour. It actually exerts a slight reinforcing action on rubber.

Antimony Sulphides. Antimony sulphides are extensively employed in rubber manufacture. The composition of different grades varies considerably, containing both antimony trisulphide and antimony pentasulphide. The former preponderates in most types, while there may be free sulphur present, ranging up to the considerable proportion of 30 per cent. Colours obtained with the different products range from yellow, through orange, to dark red. Antimony sulphide is

non-toxic and for this reason has always been very popular for rings for bottles, and for rubber products which have to come into contact with food.

There is a wide variety of inorganic materials which are employed to give different colours to rubber. They are being largely displaced by organic pigments. But until vulcanizing conditions moderated to favour the latter, nearly all colours were supplied by these fillers. Yellows are obtained by using arsenic sulphides and cadmium compounds, while zinc chromate has been used. Green was generally developed by means of chromium oxide. Ultramarine and prussian blue give blue shades. Unfortunately all these colours tend to fade during hot vulcanization and lose any brilliance of shade.

Organic Dyestuffs. Colour is now generally conferred on rubber by the use of organic dyestuffs. Much smaller quantities need to be used than is the case with mineral pigments. Brilliant colours of every shade may be obtained. In many cases the dyestuffs are such as to exert a protective action on the final products.

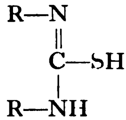
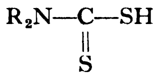
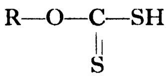
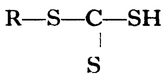
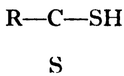
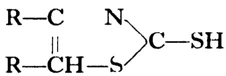
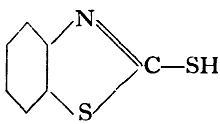
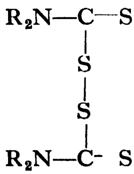
Accelerators

What are Accelerators? Accelerators are chemical compounds which, added to rubber mixes prior to vulcanization, hasten the rate of vulcanization. They are effective in varying degrees in synthetic rubbers. There are a number of types of these materials, differing in the extent to which they effect vulcanization. Whereas even thirty years ago it took several hours for vulcanization at a temperature of 140° C., now far superior products are obtained in a few minutes, even seconds, at temperatures below the boiling-point of water. Various inorganic materials have been known from the time of Hancock to have an accelerating effect, but prime interest at the present time is concerned with organic compounds.

Table 83 shows the main types of organic accelerating materials.

Rubber and sulphur mixed together require to be heated at 140° C. for about five hours in order to obtain a technically useful vulcanized rubber. When zinc oxide is added to the original mixing, then the best vulcanized product is obtained in an hour less, under the same conditions. If, now, the experiment is repeated with additions of one of the earliest accelerators, thiocarbanilide, using about 1 per cent., then the best product, still employing the same temperature, is obtained in about two hours. Substituting thiocarbanilide, by a modern fast accelerator, mercaptobenzthiazole, the time taken is now half an hour, at 140° C. But when this accelerator is mixed into the rubber on the mixing-mill, a difference is soon noticeable, for if the material is allowed

TABLE 83. TYPES OF ACCELERATORS

Thioureas	
Thiophenols	
Mercaptans	R_3C—SH
Dithiocarbamates	
Xanthates	
Trithiocarbamates	
Dithio acids	
Mercaptothiazoles	
Mercaptobenzthiazoles	
Thiuram disulphides	

to become too hot, it tends to " scorch " or " set-up ". In other words, the accelerator is already becoming active at this low temperature. Lower sulphur content is necessary, coming down from 8 per cent. to about 3 per cent. Typical of even faster ultra accelerators is zinc dimethyldithiocarbamate. One per cent. incorporated into the rubber-sulphur-zinc oxide compound gives a product which will set-up in a few seconds at 140° C. It will give a vulcanized product in a few minutes at the much lower temperature, 120° C. What is more, it will

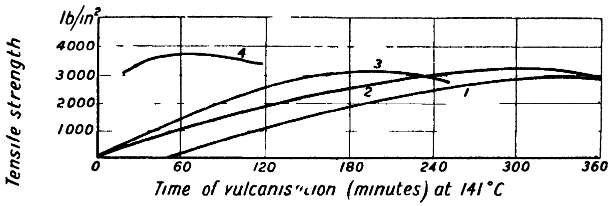


FIG. 54.—Decreasing Time required for Vulcanization with Modern Compounding.

even give a fully vulcanized material on standing at ordinary temperature. Nor is this all, for another type of fast accelerator will vulcanize rubber without using any sulphur at all. Thus 3 per cent. of tetramethylthiuram disulphide in the original mixing will give a fine vulcanized product in about twelve minutes at 140° C. There are also accelerators which are too fast in action to be handled on mixing mills, and whose use is at present confined to the vulcanization of latex.

Fig. 54 illustrates the decreasing time required to vulcanize rubber. Mixes 1 and 2 are primitive types. Mix 3 is a pre-war type, while mix 4 is an up-to-date rubber.

TABLE 84. TYPES OF MIXES EMPLOYED

	1	2	3	4
Rubber	100	100	100	100
Sulphur	8	8	6	3
Zinc oxide		5	5	5
Aniline			2	
Mercaptobenzthiazole				1
Stearic acid				1

Development of Organic Accelerators. The use of organic accelerators as at present practised became quite general and systematic only after 1920. It is interesting to trace their development.

In 1880, Rowley [17] employed ammonia to vulcanize rubber, although he was more interested in using it for " blowing " sponge rubber. The fact that certain inorganic materials, such as lime, litharge and zinc

oxide, hastened vulcanization was quite well known. Weber's impression that the inorganic accelerators acted by virtue of their basic character was subsequently shown by Gottlob [8] to be incorrect, because quite strong alkalis such as barium and strontium oxides had no effect, whereas the closely related calcium oxide had a pronounced effect.

The really profound development, the birth of organic accelerators, was made in 1906, by Oenslager.[13] The discovery, although kept secret, was worked for many years. He discovered that aniline and other organic materials, notably thiocarbanilide and hexamethylenetetramine, profoundly hastened vulcanization. Although the initial object was to overcome the variability of rubber, it soon became evident that the products were far superior as regards physical properties. Aniline proved to be so toxic, that after a number of years it was displaced by *p*-aminodiphenylaniline, the effect of which was discovered by Spence.

In 1912 the Bayer Co., Hofmann and Gottlob [2] obtained a patent for the use of piperidine as an accelerator of vulcanization. This was followed shortly afterwards by a patent covering organic bases having a dissociation constant greater than 1×10^{-8}. Within a few years combinations of aliphatic bases with carbon disulphide to form dithiocarbamates began to attract much attention. It was after this time that the search for accelerators of vulcanization became frenzied. In 1919 yet another type of very fast accelerator came into being when the effect of tetrathiuram disulphide was discovered. Shortly after this Bruni and Romani [3] made the profound discovery that this accelerator could function without adding any sulphur at all. About the same time one of the most popular accelerators, diphenylguanidine, familiarly known as DPG, was introduced to the rubber industry. It came in to replace the slow tricarbanilide and hexamethylenetetramine. Although only moderately fast in action, it was so easy to handle and so amenable that it immediately attained a remarkable popularity, which has been maintained. With this came related materials such as diorthotolylguanidine which gave delayed acceleration, a very useful property in certain circumstances. A few years later, in 1925, mercaptobenzthiazole came into use and rapidly became the most extensively used accelerator of any. It has an equal significance for GR-S.

In recent years much effort has been devoted to working out further the chemical themes suggested by these different compounds. Hexamethylenetetramine has been displaced by the homologous aldehyde-amine. Different aldehydes such as acetaldehyde, butyraldehyde, and aliphatic bases have been employed instead of ammonia. Sulphur-containing materials, mainly carbon disulphide derivatives, are the

outstanding type of accelerator at present. Thiocarbanalide has given place to the dithiocarbamates and mercaptobenzthiazole. New combinations incorporating carbon disulphide to secure the dithiocarbamate grouping are being evolved on every conceivable theme. Intense activity is also noticeable in the production of very fast accelerators, some water-soluble, others insoluble, which will function rapidly in latex.

No sooner was it realized that accelerators of the dithiocarbamates type were more powerful in the presence of zinc oxide, than metallic radicals began to replace the basic portion. Zinc, lead and cadmium compounds are now available, offering a varying range of properties. From using single accelerators, the tendency is to employ more than one in order to improve control of vulcanization. Small percentages of ultra-accelerators of the dithiocarbamate type are found to enhance or boost the speed of vulcanization achieved with milder, less fierce, accelerators.

Rubber when vulcanized acquires a number of very important advantageous properties which have already been described. But if the mixing is of the primitive type containing only rubber, sulphur, and zinc oxide, it still has a number of disadvantages. It vulcanizes very slowly, its physical properties are still not good enough, and it perishes very easily. As faster and faster accelerators came into use, the proportion of sulphur required dropped steadily, and the time of cure became shorter and shorter. A number of other effects became apparent. Not only were the physical properties considerably enhanced, but the rubber took a much longer time to deteriorate—it aged much better. It became apparent that to obtain the very best out of vulcanized rubber, fast accelerators were desirable, involving a low proportion of sulphur and giving a rapid cure. Another great advantage was that by enabling such low amounts of sulphur to be used, there was little free sulphur available for further vulcanization to occur. Consequently rubber products have become much more resistant to heat.

Dinsmore and Vogt[6] have endeavoured to classify accelerators according to their speed and their other effects on rubber. Their results are shown in Table 85.

Inorganic Accelerators. From the time when vulcanization was first practised, rubber manufacturers were up against difficulties. Although vulcanization improved their products, yet it was difficult to control. The chief difficulty was, of course, when it would not work at all. Fortunately there were means of overcoming this. In his vulcanization patent, Goodyear[9] mentioned the use of basic lead carbonate as a pigment. It was soon discovered that this, together with a number of other materials, hastened the vulcanization. The

TABLE 85. CLASSIFICATION OF ACCELERATORS

	Pure gum mix			
	Softening	Modulus	Tensile	Activity
1. Dithiocarbamates	None	High	High	2
2. Xanthates	N	H	H	1
3. Thiuram sulphides	N	H	H	3
4. Mercaptobenzthiazole	Slight	Low	Low	6
5. Vulcanol	N	H	H	7
6. Aldehydamines	S	H	H	8
7. *p*-Nitroso dimethylaniline	S	L	L	5
8. Ethylidene-aniline	S	L	L	9
9. Aldehydeammonia	N	L	L	10
10. Guanidines	N	H	H	11
11. Hexamethylenetetramine	N	H	H	12

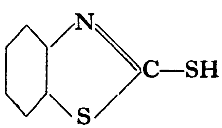
most important were lime, magnesia, zinc oxide and litharge. For example, Fanshawe [7] used a mixing of rubber, sulphur and litharge. Suitable additions of these would often enable stubborn rubber to vulcanize. In many cases, however, vulcanization simply could not be brought about. In current practice inorganic accelerators have been almost entirely superseded by the organic types.

Magnesia. Made by heating magnesium hydroxide or carbonate, this is obtained in two forms as light calcined magnesia or as heavy calcined magnesia. The former, specific gravity 3·2, has fine amorphous particles, while the latter, specific gravity 3·65, has distinctly needle-like crystals. Magnesia has been shown to have a profound accelerating effect on vulcanization.

Litharge. Litharge has a very high specific gravity and is obtained in two forms, red and yellow. An effective accelerator of vulcanization, it is still widely employed. It can only be used for dark products because, during vulcanization, invariably the characteristic black lead sulphide is formed. It exerts a distinct reinforcing effect. A particular application is for protective rubber for radio-active work. One such material contains PbO 90 per cent.; rubber 9 per cent.; S 1 per cent. Litharge is quite extensively used for footwear, insulators, brake linings, etc.

Examples of Organic Accelerators.

Mercaptobenzthiazole



Mercaptobenzthiazole is the outstanding accelerator of the day. Almost certainly the most widely used, it has undoubtedly been the greatest influence in establishing modern rubber practice with its low sulphur ratios, low curing temperatures, and improved physical properties. It is very effective in GR-S and in Perbunan types serving as a medium speed accelerator.

It is a yellow powder melting when pure at 176° C. Its specific gravity is 1·42. It has an easily recognizable pungent odour and a bitter taste, which it imparts to products containing it. Being non-toxic, it is quite safe to handle. Insoluble in water, it is soluble in alkalis, alcohol, acetone, ether and benzene.

Mercaptobenzthiazole requires the presence of zinc oxide and stearic acid to function to best advantage. Examples of its use are:

Tyre tread		*Inner tube*	
Rubber	100	Rubber	100
Pine tar	2	Stearic acid	1
Stearic acid	4	Antioxidant	1
Zinc oxide	5	Zinc oxide	10
Antioxidant	1	Sulphur	1
Carbon black	50	Mercaptobenzthiazole	1
Mercaptobenzthiazole	1·25	Tetramethylthiuram disulphide	0·25
Sulphur	3		
Mineral oil	1		
Vulcanized 30 mins. at 40 lb. per sq. in.		Vulcanized 20 mins. at 50 lb. steam pressure	

It is regarded as a semi-ultra accelerator. For rubber mixings containing little filling material, about 1 per cent. on the rubber is usually employed, increasing to 1·5 per cent. where heavy loadings are employed. The amount of sulphur usually added is between 2·0 per cent. and 3·5 per cent., the latter being employed where absorbent fillers such as carbon black or clay are used.

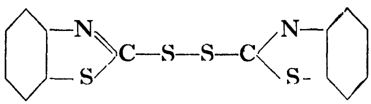
Mercaptobenzthiazole begins to act at quite low temperature, which accounts for its tendency to cause pre-vulcanization on the mixing mill. Thus it will vulcanize an ordinary mixing in several hours at 100° C., in less than two hours at 120° C., half an hour at 140° C., and in a few minutes at 160° C.

It must be borne in mind in compounding that mercaptobenzthiazole is activated by the presence of alkaline materials and tends to "scorch" or "set-up" the mix. Consequently alkali reclaim, ammonia, etc., as well as certain other materials such as diphenylguanidine, urea, and magnesium carbonate, must be used with care. Other features which commend it are its ability to withstand light and the fact that it does not discolour a mixing. It also gives a high modulus

right through all stages of vulcanization. It has a profound retarding effect on ageing.

The leading German accelerator was Vulkacit A2, which was a combination of mercaptobenzthiazol and diethylamine. This was widely used for natural rubber and for the various Buna types.

The tendency for scorching has resulted in a trend for using derivatives of mercaptobenzthiazole, having all its advantages without this particular disadvantage. One which successfully realizes these objects is dibenzthiazyl disulphide:



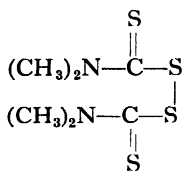
Diphenylguanidine

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \Big\rangle NH$$

This is one of the most widely used accelerators. It is a white crystalline powder melting at 145° C. and having a specific gravity of 1·1. It is odourless, non-toxic, and shows little tendency to scorch during mixing. Zinc oxide is necessary for this accelerator to function, although it may be replaced by litharge or magnesia. From 0·5 to 1 per cent. of diphenylguanidine is employed in a rubber mix with 3·5 per cent. of sulphur. Although rubber products in which it has been used are very strong and tough, it does not assist their ageing. For this reason it is losing ground. It is relatively ineffective in GR-S.

Sulphenamides have become very popular for accelerating vulcanization of natural rubber and synthetic rubbers.

Tetramethylthiuram Disulphide

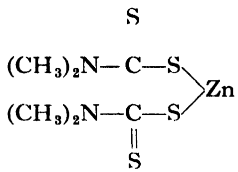


This is a greyish powder, melting at 154° C. It is soluble in benzene, carbon disulphide, chlorinated solvents, and acetone, but is almost insoluble in petrol, alcohol and water. It is non-toxic, has a typical odour and does not discolour compounds containing it. Vulcanization can be achieved without employing any sulphur, since when it decomposes it supplies sulphur in a very active form. In this

case about 3 to 4 per cent. on the weight of rubber must be added. This accelerator is employed where exceptionally good ageing and heat resistance are required. In ordinary mixes up to 1 per cent. is used together with from 1 to 3 per cent. of sulphur. A very fierce accelerator, it is liable to cause the rubber to " scorch ". It finds considerable application as a secondary accelerator in quantities of about 0·1 per cent. to aid standard vulcanization. This class of accelerators is very useful in synthetic rubbers. It is particularly effective in Butyl rubber (GR-I).

The corresponding monosulphides are also useful in natural rubbers and synthetic rubbers.

Zinc Dimethyl Dithiocarbamate



This accelerator is considered as being typical of the group of very fast accelerators which are salts or compounds of dithiocarbamic acid. The methyl groupings can be replaced by other groups such as ethyl, propyl, and so on. It is a white powder melting at 250° C., having a specific gravity of 2·0. Relatively insoluble in most solvents, it is non-toxic, and does not discolour the rubber. It is an exceedingly active accelerator, promoting vulcanization well below 100° C. It is so fast as to be difficult to handle on the mixing mills or in processing. Alone, it is used for a few minor purposes, other than in latex, for which it is one of the most popular and effective accelerators. It is finding increasing employment as a secondary (or boosting) accelerator, in amounts generally of the order of 0·1 per cent., to aid the primary accelerator (such as mercaptobenzthiazole).

Some Valuable Properties of Accelerators. Certain properties are keenly sought in accelerators. Among these are effects known as the " plateau effect " and " delayed action ".

Plateau Effect. As the time of vulcanization of a product is increased, so the tensile strength increases until it reaches a maximum value. Before this the product is regarded as under-vulcanized. After this stage, in the normal way the tensile strength decreases and the rubber is on the way towards being over-cured. With certain accelerators, however, this optimum tensile strength is maintained over a considerable period of time. For example, if optimum properties

are obtained in 30 minutes at 140° C., then with an accelerator showing plateau effect, the properties of products obtained in 25 or 35 minutes will not be appreciably different. This allows a vulcanizing margin of 10 minutes during which products will not be spoiled. The effect is shown by a flattening-out of the curve representing tensile strength against time of vulcanization. For this reason it is known as the plateau effect. The margin of safety which the use of such an accelerator gives in manufacture is invaluable.

Mercaptobenzthiazole is an example of an accelerator showing a particularly good plateau effect. Fig. 51 shows the difference between this (B) and an accelerator displaying a well-defined tensile maximum (A).

Delayed-action Accelerators. The chief difficulty relating to the use of accelerators in rubber is the tendency for "scorching" during processing or during storage prior to vulcanization. It comes about because the accelerator acts too rapidly, incipient vulcanization commencing at the low temperatures employed. The difficulty has always been to find accelerators which will not tend to scorch, but yet will give the desirable rapid accelerating effect. This has been achieved by the use of what are known as delayed accelerators. They will not scorch at processing temperatures and are foolproof. Yet at vulcanizing temperatures they are exceedingly fast. Among the best known are diorthotolylguanidine and many aldehyde-amine compounds.

These accelerators are very useful when thick articles are being vulcanized, where, owing to poor heat conductivity, the interior tends to lag behind in temperature. They are also convenient where rapid set-up of rubber is not desired, and in cases where appreciable flow of rubber is wanted.

Antioxidants. An antioxidant may be defined as "A substance which increases the life of rubber mainly by its influence in delaying oxidation". It is interesting that the trend for use of antioxidants only became apparent because it was made quite clear that accelerators themselves were having a profound retarding effect on ageing. Since this only applied to certain classes of accelerators it became apparent that the introduction of new organic materials based on these might have a similar effect.

Many chemicals were known which, because they absorbed oxygen, had beneficial effects on other materials. For example, pyrogallol and hydroquinone are well-known absorbents of oxygen. However, although materials of this type undoubtedly assisted to retard the ageing of vulcanized rubber, at the same time they retarded the rate of vulcanization, which was not so good. In recent years a number

of materials have been found having specific and very marked antioxidant properties, while not affecting the rate of vulcanization of the rubber.

Before describing some of them it may be as well to point out the desirable properties of a good antioxidant.

1. The material should be easily dispersable in the rubber and easy to handle.
2. It should be inert so far as vulcanization is concerned, neither retarding nor accelerating.

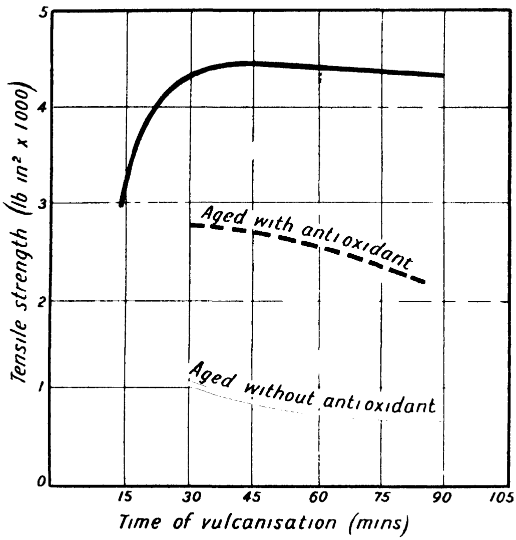


FIG. 55.—Influence of Antioxidants on Rubber.

3. It should not have any effect on the colour of the vulcanized product.
4. It should be non-toxic.
5. It should have a beneficial effect on vulcanized rubber when subjected to every type of stress.

Classification of Antioxidants. The chief types of materials specifically employed for their antioxidant effects are:

1. Phenols, such as pyrogallol and hydroquinone, and aminophenols.
2. Aldehyde-amine condensation products such as acetaldehyde-aniline and aldol-α-napthylamine.
3. Secondary naphthylamine derivatives such as phenyl-α-naphthylamine, and phenyl-β-naphthylamine.

4. Ethylene diamine derivatives such as phenylene diamines.
5. Aromatic diamines such as the tolylamines.
6. Ketone-amines.

Some Examples of Antioxidants. The following examples describe some of the most popular antioxidants.

1. Aldo-α-naphthylamine is a reddish, resinous product. It has a specific gravity 1·16, and a characteristic odour. Although insoluble in water, it dissolves in benzene, alcohol, and chloroform. It disperses quite easily in rubber. In general it has only a very slight effect on acceleration. Used in amounts up to 1 per cent., it is effective against deterioration by heat and oxidation.
2. Phenyl-β-naphthylamine is a grey powder, whose specific gravity is 1·19, and which melts at 160° C. It is insoluble in water and alcohol, but dissolves in benzene and carbon disulphide. If used in proportions greater than 2 per cent. it tends to bloom. It disperses quite easily in rubber, and does not stain vulcanized products, although staining appears when the products are exposed to sunlight.

The outstanding disadvantages of antioxidants is the fact that nearly all of them tend to discolour light-coloured vulcanized products. It is interesting to notice that this effect has been assumed to be one explanation for their antioxidant behaviour.

TABLE 86. EFFECT OF ANTIOXIDANT ON A TYRE TREAD

Tyre tread	
Rubber	100
Stearic acid	4
Pine tar	2
Zinc oxide	5
Carbon black	45
Sulphur	3
Aldol-α-naphthylamine	1
Mercaptobenzthiazole	1

	Vulcanized 25 minutes at 40 lb./in.²		After 7 days Oxygen bomb.	
	T_B	E_B	T_B	E_B
Without antioxidant	4,400	610	620	360
With antioxidant	4,450	620	2,425	530

Phenyl-β-naphthylamine is by far the most important antioxidant used in synthetic rubber technology. Nearly all types contain about 2 per cent. Actually it serves a dual purpose. It is added at the end of polymerization in the case of GR-S and Buna S3. Its functions are to stop the polymerization and to stabilize the finished rubber. Thereafter it performs its usual function as an antioxidant.

REFERENCES

[1] BARNETT, *Ind. Eng. Chem.*, 1934, **26**, 303.
[2] Bayer Co., HOFMANN and GOTTLOB, G.P. 266,619/1912.
[3] BRUNI and ROMANI, *I.R.J.*, 1921, **62**, 89.
[4] BURBRIDGE, *Trans. I.R.I.*, 1926, **1**, 429.
[5] CRANOR, *Rubber Chem. Tech.*, 1943, **16**, 695.
[6] DINSMORE and VOGT, *Trans. I.R.I.*, 1928, **4**, 85.
[7] FANSHAWE, B.P. 9,189/1841.
[8] GOTTLOB, *Gammi-Z.*, 1916, **30**, 303.
[9] GOODYEAR, *Gum Elastic and Its Varieties*, New Haven, 1853.
[10] GREEN, *Chem. Met. Eng.*, 1923, **28**, 53.
[11] GRENQUIST, *Ind. Eng. Chem.*, 1929, **21**, 667.
[12] LLOYD, *Trans. I.R.I.*, 1927, **3**, 52.
[13] OENSLAGER, *Ind. Eng. Chem.*, 1933, **25**, 232.
[14] PARK, *Ind. Eng. Chem. (News)*, 11, 1933.
[15] PARKES, B.P. 11,147/1846.
[16] PARKINSON, *Rubber Chem. Tech.*, 1944, **17**, 473.
[17] ROWLEY, B.P. 787/1880.
[18] WEBER, *Loc. cit.*, p. 214.
[19] WHITBY, *I.R.J.*, 1924, **68**, 617.
[20] WIEGAND, *Canadian Chem & Proc. Ind.*, 1944, **28**, 151.

CHAPTER 12

ELASTOMERS—BUTADIENE TYPES

It seems quite clear from the previous discussion that more work has been based on butadiene than on any other monomer. There can be no doubt that elastomers based on butadiene lead the way in respect to output. Furthermore, the production on a vast scale in the United States is for the main part likewise based on butadiene.

In the United States, GR-S and butadiene-acrylonitriles are the leading productions based on butadiene, while butyl rubber also contains a minor proportion of this material. Until 1942 the best-known materials were Buna-S, Perbunan, and the slightly modified Perbunan-Extra. The former predominates, since it is the material used for tyres. These are the leading types manufactured in Germany. In the U.S.S.R. two leading types of synthetic rubber, namely, S.K.A. and S.K.B., are also made from butadiene. All of these materials (with the exception of the Russian types, and butyl rubber) are copolymers of butadiene with synthetic resin monomers. The most extensively used synthetic resin monomer is styrene, which goes into the Buna-S, while acrylic nitrile and other acrylic derivatives are used in the other materials. Modified types of neoprene and of Thiokol are also largely composed of butadiene.

The German rubbers, Perbunan and Perbunan-Extra, had been exported for some years before the war, and there is a wide experience of them. They had gained considerable popularity in Great Britain and in the United States for their oil-resisting properties.

GR-S is the outstanding type in the United States. The Government made this the standard material. It is also made under several proprietary names, including Buna-S, Butaprene-S, Chemigum, Hycar, Buton-S, etc.

The Russian materials S.K.A. and S.K.B. have been in large-scale production for a number of years.

All these materials have the general properties of natural rubber. They are rather more difficult to process than rubber, but they can all be handled on standard rubber plant. According to the original German technique Buna-S does require a certain amount of special equipment. As a result of tremendous technical work this is no

longer the case elsewhere. In general, the procedure is the same as with rubber, namely, they are brought into a thermoplastic condition when compounding ingredients may be incorporated. The addition of sulphur and accelerators, followed by a heat treatment, converts them from the plastic condition into the elastic state corresponding to vulcanized rubber. Indeed, it is an extremely difficult task to differentiate between such products and comparable rubber products.

Obviously the ability to handle these materials on established rubber plant is a contributory factor to their continued success. In view of the enormous amount of capital sunk in such plant this is essential to their commercial success. In many respects they yield products which are far superior to natural rubber products; in some properties they are no better than rubber; they are, of course, still much dearer, although the gap is being rapidly narrowed.

Butadiene Rubber. According to the United States Bureau of Commerce, the Russians in 1939 produced 60,000 tons of synthetic

$$\underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \longrightarrow \begin{array}{l} -CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH \\ \quad {=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2{-}CH_2{-} \end{array}$$

Polymerized butadiene
(probably cyclized to a considerable extent)
S.K.A., S.K.B., Buna 85, Buna 115, etc.

FIG. 56.

rubber. A considerable proportion of this production consisted of sodium-polymerized butadiene. It is referred to as divinyl rubber. The U.S.S.R. appears to be the only producer of straight butadiene elastomers, which approximate most closely, at least in chemical composition, to natural rubber. They have undoubtedly developed the technique of sodium polymerization to a very high pitch. There is an enormous volume of scientific and technical literature on the subject, although so far there has been no independent appraisal of the merits of the products. Not a great deal has as yet been heard about any of their copolymerized products, although there is evidence that these are being manufactured. On the other hand, it is known that they manufacture a chloroprene rubber, i.e. similar to neoprene, which they call Sovprene, and they also make olefine polysulphide rubbers. There is no doubt that sodium-polymerized butadiene, known as S.K.B., is the predominant type.

S.K.B. is made from butadiene, which has been obtained from alcohol, while S.K.A. is made from butadiene which has been derived from petroleum. Some indication of the extent to which these materials have been used, and still are used, is obtained from

consideration of the great importance attached to the reclamation of sodium-butadiene rubber. The amount of attention which has been devoted to this is a measure of the existence of a large amount of material to be reclaimed.

It is to be presumed that these sodium-polymerized rubbers have many features in common with Buna 85 and Buna 115, the comparable German types. Buna 115 is obsolete and is no longer used. Buna 85 has found fairly wide usage. The Russians confirmed the excellent opinion expressed by the Germans about the suitability of sodium-butadiene rubbers for hard products. The heat resistance and mechanical properties are far better than those of comparable ebonites.

S.K. is not oil-resistant, although only approximately one-half of its weight is soluble in benzene. It resists oxidation to a remarkable extent. Heating and mechanical working (milling) have practically no effect on its plasticity.

Like other butadiene polymers or co-polymers, S.K. synthetic rubber lacks sufficient " building tack ", and considerable effort has been expended by Russian technologists to remedy this, one of the more successful ways being the combine used of phenylhydrazine and a softener, such as rosin.

This is of particular importance in the case of " built-up " articles, such as rubber footwear. Success has been achieved by a number of expedients, e.g. by reducing the number of parts in a shoe, and the extensive use of shaped diaphragm presses.

The performance of articles made from Russian S.K. rubber in actual usage, e.g. tyres, cannot be conclusively judged without bearing in mind that a number of factors are *a priori* operating against it. Russian carbon blacks are inferior to American brands, and as is well known, the mechanical properties of all butadiene polymers are extremely sensitive to the quality of the carbon black used. Russian tyre cord is inferior, and the design of Russian tyres is, or at least two years ago was, by admission, lagging behind American tyre designs and constructions of the day. Accordingly, the only comparison that can be made is between Russian tyres made from 100 per cent. S.K. rubber with Russian tyres made under identical conditions from 100 per cent. natural rubber. It has been stated that, in actual road service, the mileage performance of all-synthetic tyres lags on the average only some 15 per cent. behind natural-rubber tyres.

The Numbered Buna Rubbers. It can be assumed that Buna 85 and Buna 115 have some properties in common with the Soviet products. In actual fact, Buna 85 is polymerized by means of potassium. It is used in making hard rubber having excellent chemical resistance and

high heat stability. The physical and ageing characteristics of compounds loaded with carbon black are shown in comparison with the comparable rubber mix in Table 87.

Processing of S.K.B. It appears that the adhesive properties of these types of synthetic rubbers are quite inadequate for the production of soft rubber articles in the ordinary way. Special treatment is necessary in order to facilitate compounding and processing.

One method for carrying this out, described by Osipovsky,[7] was to heat the material at 140° C. in air, and in this way to reduce it to a more thermoplastic condition. Another method was the use of agents having a powerful depolymerizing action, a notable one being para-nitroso dimethylaniline.

TABLE 87. PROPERTIES OF RUBBER, BUNA 85 AND BUNA 115

	Natural rubber	Buna 85	Buna 115
T_B Kg. cm.^{2}	260	175	200
E_B %	600	600	700
Shore hardness	65	65	60
Geer oven			
(32 days at 90° C.) T_B	160	155	170
E_B	350	600	625
Oxygen bomb			
(32 days at 60° C.) T_B	50	150	180
E_B	200	620	650

Vulcanization of sodium-butadiene rubber compounds could be quite satisfactorily carried out without the use of sulphur. Oxidizing agents facilitate the process, notably benzoyl peroxide which when present to the extent of 3 per cent. effectively enabled the vulcanization of a typical compound in 15 minutes at 150° C.

The composition and tensile properties of a typical compound based on S.K.B. are shown in Table 88.

In regard to sodium-butadiene rubbers the effect of accelerators is only to shorten the time and lower the temperature for combination with sulphur. The products show no qualitative benefits over straightforward vulcanization with sulphur. Zinc oxide is necessary with accelerators. In the presence of stearic acid, calcium oxide and magnesia accelerate the vulcanization. Thiuram derivatives are effective and improve heat resistance. The normal range of antioxidants function satisfactorily.

Softening Agents for Mixtures of Sodium-butadiene Rubber. Segalevitch[8] has studied the effects of more than 100 softening agents

in mixtures prepared from butadiene rubber. He considered the effects both on the properties of the raw mixtures and on the properties of the mixtures after vulcanization. Seven softening agents gave particularly good results: (i) a polymerized naphtha-resin product, prepared by polymerization of unsaturated compounds from the reaction of light oil and aluminium chloride, imparted considerable tackiness, aided the processing of the raw mixture, and improved the

TABLE 88. TENSILE PROPERTIES OF TYPICAL S.K.B. COMPOUND

Compound	
Synthetic rubber (plasticity 0·040)	100
Gas black (Baku)	50
Sulphur	4·0
Accelerator	1·0
Softener No. 2	3·0
Zinc oxide	4·0
Softener No. 3	5·0
Tensile properties	
Vulcanization (mins. at 150° C.)	20
T_B (kg. per sq. cm.)	100
E_B (%)	555
Permanent set (%)	60

mechanical properties of the vulcanizate before and after ageing; (ii) the furfural extract from the purification of naphtha oils improved processing and the mechanical properties after vulcanization; (iii) the extract from the purification of naphtha oils with propane and cresol improved processing and mechanical properties of the vulcanizates; (iv) soft asphalt, and Ischimba asphalt improved processing and the mechanical properties of the vulcanizates, including the heat resistance of the latter; (v) soft asphalt from Binagadin, Bibi-Eibat, and Gorjki; (vi) polymers from the oxidative cracking of Dubrowawa were of particular interest because of improved resistance to abrasion of the vulcanizates; (vii) esterified castor oil.

Dogadkin and Fel'dshtein[2] examined the vulcanization characteristics of sodium butadiene rubber containing various proportions of carbon black, chalk, kaolin, and silica, before and after being heated within the temperature interval of 70°–200°. Large percentages of fillers caused limited swelling of the unvulcanized rubber. They considered that the limited swelling is due primarily to the structure of the system. The rubber comprises the discontinuous disperse phase and the filler forms the continuous phase producing a singular net-like structure with the rubber sealed inside the cells. Heating of the mixture reduced the proportions of fillers necessary to produce limited swelling

and also caused limited swelling of the rubber itself, but in the latter case longer periods of heating were necessary. Heating at 120°–140° C. produced the following changes which are characteristic of vulcanization: limited swelling, decreased solubility, and greater toughness. The synthetic rubber mixtures were vulcanized without sulphur by heating at 190°–200°. Under identical conditions smoked sheet mixtures could not be vulcanized. It is believed that "vulcanization" proceeds as a result of (i) interaction between the rubber and the oxygen absorbed on the rubber and the fillers, and (ii) thermal condensation of the rubber hydrocarbon.

Kusov[5] described the products obtained at 200° C., using large quantities of carbon black as filler. Material having tensile strength of 90 kg. per square centimetre and elongation at break of 400 per cent. was obtained.

There are many indications that these sodium butadiene rubbers are used in the manufacture of tyres, and according to Lebedev[6] the products have far superior abrasion resistance than the comparable rubber stocks. Other references discuss the application of sodium rubber for impregnating fabrics for making soles and heels and a wide range of mechanical goods. Gagina[3] has discussed in some detail the excellent results obtained by using sodium butadiene rubber in tyres.

Importance of Reclaiming. One of the favoured methods for reclaiming these materials for further use is to swell the products in solvents with heating, and thereafter to remove the solvent. The product could be used quite successfully for lower-grade articles.

The physical and chemical properties of the reclaimed rubber obtained by the solution method have been found satisfactory. Experimental trials carried out at an artificial rubber sole factory with the products are reported to have demonstrated that soles can be manufactured entirely from the reclaimed article. So far, the rubber reclaimed from used synthetic rubber (mostly automobile tyres) has been utilized in the manufacture of rubber soles and of artificial leather. The present Soviet output of reclaimed synthetic rubber is not large, but the favourable results thus far obtained are stated to have dispelled any doubt of the practicability of the utilization of this method for the production of reclaimed synthetic rubber on an industrial scale.

The Russians have prepared chlorinated derivatives from S.K. rubbers. Koshelev, Provorov, and Solovieva[4] have described the conditions. Solution of 7 per cent. divinyl rubber in dichlorethane were best with 3·5 kilograms of chlorine per kilogram of rubber. The final chlorine content was up to 59 per cent. The S.K. derivative could be

used as a lacquer when taken up in xylene. The products were very resistant to strong acids.

The stability of these chlorinated rubbers was not impaired by heating for 12 hours at 60° to 80° C., nor did any softening take place when the temperature was kept at 60° C., but with prolonged heating at 80° C., chlorinated S.K.B. begins to soften.

In Russia, synthetic rubber and rubber produced from native plants like *kok-saghyz*, Valochnik, and guayule, have been used as the bases for chlorinated rubber. Initial tests were made with rubber in a dry state as well as in solution, but all attempts at chlorinating dry rubbers ended in failure. Dichloroethane was found to be the best solvent for chlorination. Chlorination of the natural rubbers was accelerated by iodine, antimony chloride, and aluminium chloride. Chlorination in the presence of iodine increased the stability of chlorinated rubbers; aluminium chloride and antimony chloride increased the percentage of fixed chlorine. The resins in resinous rubbers for the most part chlorinate and eventually act as plasticizers.

Chlorination of synthetic rubbers in solutions containing iron reduced the stability and solubility of the product. Lead decreased the solubility but not the stability of the product. Both iron and lead had no effect on the amount of chlorine which combined.

As far as chlorine content and outward appearance are concerned, the closest resemblance to chlorinated plantation rubber was shown by *kok-saghyz* (55 per cent. chlorine), Sovprene (59·5 per cent. chlorine), and *bereskle*t gutta-percha (58 per cent. chlorine). Then came *eukomia* gutta-percha (54·7 per cent. chlorine) and S.K.B. (52 per cent.). Chlorinated *kok-saghyz* and S.K.B. showed the highest viscosity, so it was possible to prepare lacquers in xylene with concentrations of only 15 to 20 per cent. The other types of chlorinated rubber have much lower viscosity, and the concentration in xylene can be 30 to 40 per cent.

German Productions. *Buna 85.*[10] This is made by reacting potassium metal with butadiene in a continuous autoclave. It is essential that the butadiene be of a very high purity and must be particularly low in water content and aldehyde content.

Buna 85 is stated to be used chiefly for the manufacture of hard rubber. The material is exceptionally good for lining tanks, etc., which are exposed to free chlorine gas. Free chlorine attacks Buna S and Buna S3 probably because of the benzene nucleus in the molecule introduced with the styrene. Since Buna 85 contains no styrene or other aromatic compounds, it is much more resistant to chlorine.

In previous manufacturing experience with Buna 85 and Plasti-

cator 32 at Ludwigshafen considerable difficulty was experienced in controlling the reaction which may become so rapid as to result in quite violent explosions. The procedure was modified following this experience.

A suspension of potassium metal in Plasticator 32 is first made containing approximately 10 per cent. of potassium. This mixture is continuously forced into the autoclave from one of two charging cylinders by means of a hydraulic ram (operated by oil under pressure from a pump). The two charging cylinders are used alternatively. The polymerized butadiene is carried forward between the screw and the inside surface of the autoclave and travels on to the end of the continuous autoclave, where it comes out through the discharge valve as a cylinder about 4 inches in diameter.

The rate of polymerization is controlled by the introduction of dioxane, 0·5 to 1 per cent. on the butadiene charged being used. It is stated that 3 per cent. dioxane would stop the reaction completely unless more potassium was used. The amount of potassium used is approximately 0·15 per cent. to 0·2 per cent. on the butadiene. The heat of the strongly exothermic polymerization reaction is removed by the cooling jacket of the autoclave and by internal cooling of the screw. Materials are forced into the polymerizer by a battery of charging pumps (small proportioning pumps)—one pumps butadiene, another dioxane, another oil to the hydraulic ram which forces in the suspension of potassium in Plasticator 32.

The crude Buna 85 coming out of the autoclave is practically gas free and is dark in colour; the colour is stated to come from the metallo-organic compound formed between potassium and butadiene. The crude product is worked up in a Werner-Pfleiderer (or Baker-Perkins) mixer, where 2 per cent. phenyl-β-naphthylamine is worked into the compound as antioxidant and fatty acid is added (1 per cent. on the crude Buna 85) to neutralize the free potassium or potash present. The material coming out of the mixer is then sheeted off on a mill, cut into sections, and packed in paper cartons.

Material consumption was as follows:

For 100 kg. of Buna 85	
Butadiene	106·00 kg.
Potassium	0·23 kg.
Dioxan	1·20 kg.
Phenyl-β-naphthylamine	2·00 kg.
Paraffin fatty acid	1 4 kg.

Buna 32 or Plasticator 32. This material is used as a vulcanizable plasticator together with Buna S and Buna S3 in the manufacture

of rubber products. The material is about the consistency of strained honey. It is produced by polymerizing butadiene with sodium powder, using a batch process in rotary horizontal autoclaves. Vinyl chloride is added to the batch. The reaction is carried out at 60° C. under a nitrogen pressure of 100 lbs./in.^{2}, over a period of 8 hours. The pressure then drops considerably and the reaction is over. A yield of about 95 per cent. is obtained.

Material consumption was as follows:

For 100 kg. Plasticator 32	
Butadiene	106·00 kg.
Vinyl chloride	0·83 kg.
Sodium	0·70 kg.

Buna 32 ebonite adheres well to many materials, metals, porcelain, wood, ebonite, plastics, etc.

TABLE 89. BUNA 32 EBONITE

Rigid		*Elastic*	
Buna 32	100	Buna 32	100
ZnO	75	ZnO	75
S	40	S	20
Thiuram	5	Thiuram	5
Lime	15	Lime	15
Dibutylamine	1		
Vulkacit P. extra	1		
Hot air cure, 1 hour at 140°–150 C.		Hot air cure, 3 hours at 180° C.	

REFERENCES

1 BREITENSTEIN, *Kunststoffe*, 1940, **31**, 73.
2 DOGADKIN and FEL'DSHTEIN, *Kauchuk i Rezina*, 1939, **12**, 12.
3 GAGINA, *Sintet. Kauchuk*, 1937, **12**, 35.
4 KOSHELEV, PROVOROV and SOLOVIEVA, *Kauchuk i Rezina*, 1939, **8**, 21.
5 KUSOV, *Kauchuk i Rezina*, 1940, **9**, 26.
—— *ibid.*, 1937, **6**, 37.
6 LEBEDEV, *Chem. Abstr.*, 1936, **30**, 5451.
7 OSIPOVSKY, *Sintet Kauchuk*, 1936, **4**, 22.
8 SEGALEVITCH, *Kauchuk i Rezina*, 1941, **6**, 4.
9 SELIVANOVA, *Kauchuk i Rezina*, 1938, **11**, 63.
10 C.I.O.S., XXVIII–13.

CHAPTER 13

ELASTOMERS—GR-S

GR-S, because it is used for tyres in the United States, is already one of the most important materials in the world. The production has rocketed to extraordinary levels. Production was 3,721 tons in 1942; 182,260 tons in 1943; in 1944 it jumped to 680,000 tons; the peak in 1945 was 725,000 tons; in 1946 it was 613,000 tons; and in 1947 the output was 409,000 tons.

GR-S has been progressively improved since the inception of the production programme. There are now a number of modified GR-S types in large-scale production accounting for about one-third of the total output. These are considered in the next chapter.

In appearance GR-S looks like a very dark brown smoked sheet and has a definite odour of styrene.

U.S. Manufacture of GR-S. The German production, although considerable, fades into relative insignificance besides the vast American enterprise. There are a number of large units spread over the United States.

Cotton [5] has recently published a description of the process carried out at the Goodyear plant at Los Angeles.

Butadiene is piped in from the Standard Oil Company's refinery 300 yards away. Autopolymerization is inhibited by addition of 50 to 200 parts per million of para tertiary butyl catechol. The liquid butadiene is stored in horizontal cylinders in the open. Before use it is found necessary to remove the inhibitor by washing the butadiene with dilute caustic soda solution, with which it is intimately mixed in a special plant, being subsequently allowed to settle out in a horizontal tank of several hundred gallons capacity.

Styrene is piped in from the adjoining Dow Chemical Co. Ten to fifteen parts per million of para tertiary butyl catechol are added as an inhibitor and it is not found necessary to wash out this small quantity. The styrene is stored in horizontal pressure vessels identical with those used for the butadiene.

Both butadiene and styrene are individually pumped from the storage tanks to the copolymerization plant, where the former is maintained under pressure.

All water used in emulsification is softened.

Sulphuric acid and brine are used to coagulate 80 per cent. of GR-S made: the remainder is coagulated with alum. Magnesium

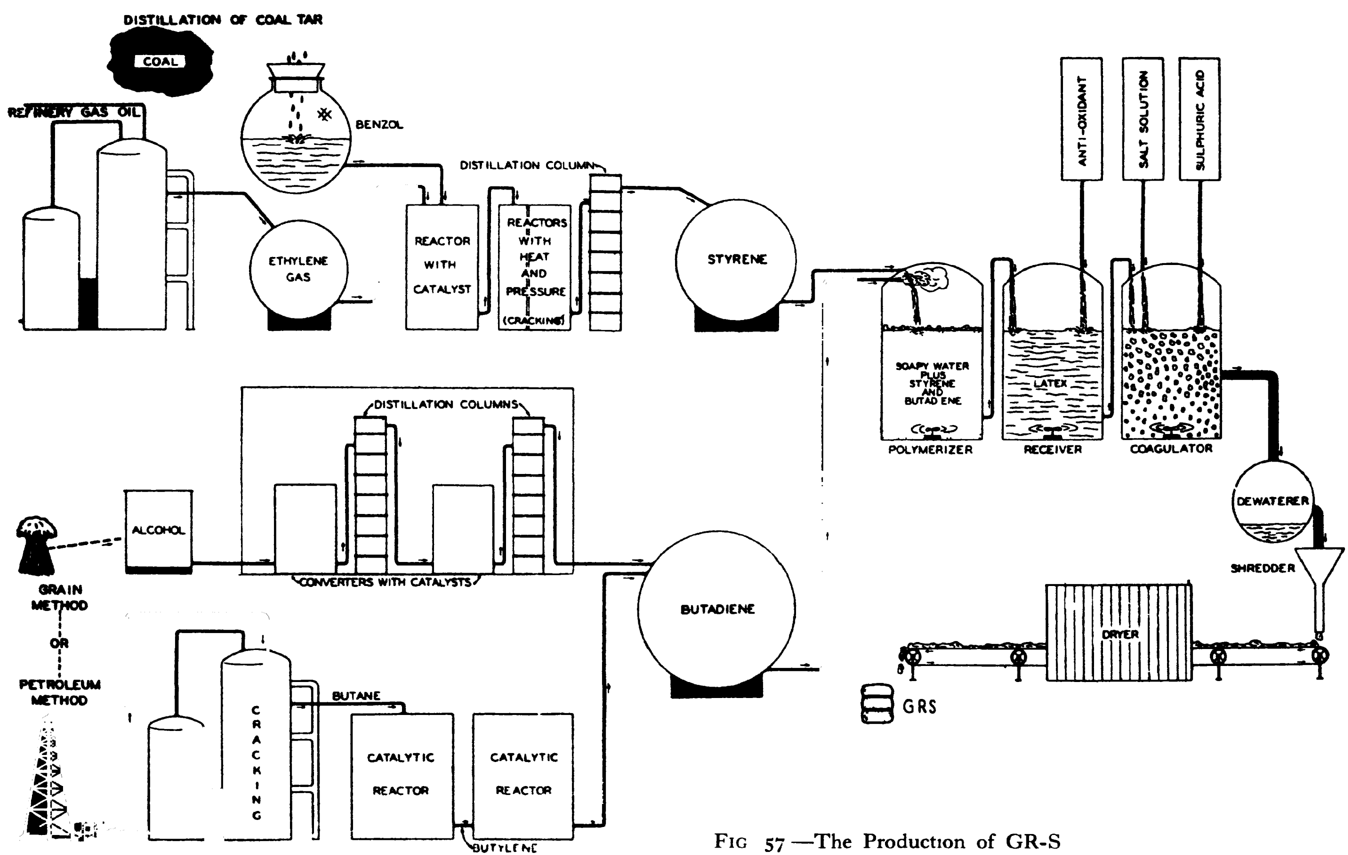


FIG 57 —The Production of GR-S

and calcium are removed from the sodium chloride by treating with a calculated quantity of hydrated lime and sodium carbonate which precipitate the calcium as calcium carbonate and the magnesium as magnesium hydroxide. After addition of these reagents the brine is allowed to settle in large wooden vats. The object of removing the calcium and magnesium is mainly to keep the ash content of the GR-S down to specification.

Dodecyl mercaptan is the preferred modifier. There has, however, been great difficulty in obtaining dodecyl mercaptan and at times it has been necessary to substitute a tertiary mercaptan. The latter makes necessary a reaction period of about 16 hours in order to reach a 72 per cent. conversion, whereas with the dodecyl mercaptan this degree of conversion is reached in about 14 hours. The amount of modifier used is between 0·45 and 0·47 per cent. on the mixed monomers.

All GR-S in this plant is produced by continuous process. (This also applies to the similar plant of half the capacity worked by the U.S. Rubber Co., on the same site, for the government.) The butadiene, styrene, soap solution containing ammonium persulphate and dodecyl mercaptan are individually delivered to a common pipeline by reciprocating pumps, each of which has a readily adjustable throw. The throw of each pump was adjusted hour by hour according to the controlled analysis of the GR-S produced. The mixed liquid passed directly to the first of twenty-four steam-jacketed reaction autoclaves of 3,750 gallons capacity, arranged in series under a roof in the open air. The emulsion in the reactors is covered with an inert gas (preponderantly nitrogen).

Each autoclave contains the standard stirring equipment and the emulsion passes continuously from one to the other along the series of twenty-four reaction vessels, taking about 14 hours. After leaving the last large autoclave the emulsion passes through a series of ten smaller vertical reaction vessels (without stirrers) of 375 gallons capacity. The emulsion passes in at the bottom and emerges from the top of each of these vessels and the hydroquinone which is used as a short stopper can be added to the emulsion in any one of these 375-gallon vessels. By this means nice control is obtained of the degree of conversion and the resulting plasticity of the GR-S produced.

After leaving the last reaction vessel the emulsion passes into a large closed cylinder where the residual butadiene is flashed off. From these the emulsion passes to one of the two multi-plate stripper columns —huge steel cylinders having a large number of horizontal perforated plates, in which the emulsion is heated under 26 inches of vacuum.

The plates in this stripper become clogged with GR-S in a period varying between 400 and 4,000 hours; so that it is necessary periodically to change from one stripper to the other and clean the one temporarily out of use.

The coagulation of the GR-S dispersion is partly a salting-out effect. Streams of emulsion, purified brine and dilute sulphuric acid were run together into a vat fitted with a stirrer. The dispersion coagulated rapidly to larger masses; *p*H was about 5. The liquor and coagulum were thrown on to the upper surface of a rotating Oliver filter covered with gauze. As the filter rotated the aggregates of GR-S were pressed under three rotating rollers and simultaneously subjected to water spray. No further washing was necessary. Only when required for electrical purposes was it necessary to subject the coagulum to prolonged washing.

The crumb from the Oliver filter was dried in a passage along a series of conveyor belts in a heated oven and then compressed into block form.

At present polymerization is taken to 72 per cent. conversion; but it has been claimed that superior properties are found in GR-S manufactured at a lower degree of conversion.

The Government-owned synthetic rubber plant at Institute, West Virginia, about 10 miles from Charleston, is one of the largest plants. It is a typical unit and is being described for this reason. It is composed of three parts: one plant of four units to produce butadiene from alcohol; one of two units to produce styrene from benzene; and the third unit to copolymerize these materials into GR-S (Buna-S). The butadiene and styrene units were designed and built and are being operated by the Carbide and Carbon Chemicals Corporation. The copolymer plant, built by the U.S. Rubber Company from plans developed by a committee of engineers, is being operated by that company.

The estimated capacity of the Institute plant is 90,000 long tons of GR-S per year. It is operated by a staff of approximately 1,250, and requires 120,000 gallons of water a minute, 14,400 kilowatts of electricity, 7,700 tons of coal a week, and 6,595 linear feet of waste disposal piping. It will represent an overall cost of $56,000,000. Its estimated production of 90,000 tons of GR-S per year may be compared to a plantation of 270,000 acres containing 24,000,000 trees.

The four butadiene units at Institute have a rated capacity of 20,000 short tons each. Alcohol, brought by railway tank cars and barges, is passed through a series of converters, the unreacted alcohol

and intermediate products being removed for recycling through the converters in a recovering system consisting of distillation towers and scrubbers. The butadiene is then purified by distilling and washing until it is over the 98·5 per cent. purity specified.

FIG. 58.—The Three "Stripping Columns" in a Recovery Unit in which excess Styrene is removed and recovered from Synthetic Rubber Latex

In the styrene production, benzol and ethylene are passed over a catalyst in an alkylator, the resulting ethylbenzene being removed from unreacted benzol in a series of fractionating columns and held in intermediate storage tanks, later being fed to a second set of reactors in which the styrene is formed. It is then purified by distillation. Both

the butadiene and styrene are pumped direct by pipe-line to the copolymer plant.

The copolymer plant is composed of three identical units, each with a capacity of 30,000 long tons per year. Butadiene and styrene, in the ratio of 3 : 1, are mixed with seven parts of soapy water in glass-lined reactor vessels. Unreacted butadiene and styrene are boiled off and

FIG. 59.—Safety Device for Synthetic Rubber Plant

One of the most interesting features of the Government-owned synthetic rubber plant in New England operated by United States Rubber Company is the safety flare pipe, seen in the background, through which excess gases escape and burn automatically. All the plant's reactors, in which butadiene, styrene, and other ingredients undergo changes that eventually convert them into rubber, are linked to the safety flare.

recovered for re-use. The emulsion is then pumped to large blending tanks, where it is mixed with other batches for uniformity. Coagulation is accomplished by the addition of salt and acid, and the coagulated particles are screened, washed, dried, and baled. The degree of conversion in American manufacture is about 72 per cent. This is considered to be rather on the high side.

Properties of GR-S. Buna-S is a copolymer of butadiene with

25 per cent. of styrene. It has a specific gravity of 0·92. It is rather tougher than natural rubber to the feel. The Government-sponsored GR-S in the United States is made of butadiene 75 parts and styrene 25 parts.

GR-S products are claimed to be far superior to rubber in heat resistance and abrasion resistance. Comparison between GR-S and natural rubber shows the following outstanding points:

GR-S

Superior in—	Inferior in—
Abrasion	Dynamic flex cracking
Ageing	Heat build-up
Reversion on overcure	Brittleness
Tendency to scorch in processing	Rate of vulcanization

GR-S compositions are used for the production of tyres, mechanical goods and cables. The rubbers obtained have high tensile strength, excellent fatigue resistance, and very satisfactory flexing resistance. They withstand the effect of sunlight and do not age as rapidly as rubber.

GR-S is a pure hydrocarbon. As a result it has excellent electrical characteristics and is extensively used both for insulation and protective sheathing of cables. Thus at 20° C. and 50 cycles GR-S has a dielectric constant of 2·9 and power factor of 0·0007. While resembling rubber in electrical characteristics, it has much better moisture resistance and retains its electrical properties at high operating temperatures for much longer periods of time. It also has good resistance towards ozone.

By contrast with the Perbunans, and most other synthetic rubber-like materials, it has no advantage whatever over rubber so far as oils and solvents are concerned.

Variability of GR-S. GR-S is being manufactured at numerous factories in the United States. Although conditions of manufacture are specified, the control is not yet tight enough to ensure that supplies from each establishment will be identical in characteristics.

This feature has been well illustrated in work aimed at electrical applications of GR-S. Thus Kemp, Ingmanson, Howard and Wallder [13] examined five samples of GR-S made at different factories. These results are summarized in Table 90. The figures show that there is still considerable variation in the materials which are coming forward.

TABLE 90. RESULTS OF MOISTURE ABSORPTION AND ANALYTICAL TESTS ON RAW GR-S ELASTOMERS

Compound	1	2	7	14	21	31	Fatty acid %	Soap %	Ash %	Water sol. in Ash %	Conductivity of Water Ext. of Ash, Mho/cm.
GR-S, A	5·8	8·8	15·9	22·5	27·2	32·2	3·92	0·78	0·82	0·772	$1·1 \times 10^{-4}$
GR-S, B	2·5	3·6	6·6	9·4	11·4	14·0	3·86	0·35	0·34	0·241	$0·36 \times 10^{-4}$
GR-S, C	5·9	8·2	15·8	22·2	26·8	31·8	3·86	0·86	1·10	0·908	$1·5 \times 10^{-4}$
GR-S, D	1·9	2·5	5·2	7·6	9·3	11·2	4·59	nil	0·57	0·541	$0·26 \times 10^{-4}$
GR-S, E	5·7	7·7	13·8	20·2	24·0	27·7	4·52	0·17	0·87	0·782	$1·2 \times 10^{-4}$
Smoked sheets	3·1	4·3	8·3	12·1	15·9	—	—	—	—	—	—

There is a specification laid down for GR-S.

GR-S as prepared already contains about 2 per cent. of an anti-oxidant such as phenyl-β-naphthylamine.

U.S. Specification for GR-S.

SPECIFICATION LIMITS.

Chemical Tests.

(*a*) Acetone extract, per cent.	10·00 maximum
(*b*) Heat loss, per cent.	0·75 maximum
(*c*) Fatty acid (as stearic acid), per cent.	3·00 minimum to 6·00 maximum
(*d*) Soap (soluble, sodium stearate), per cent.	1.00 maximum
(*e*) Ash, per cent.	1·50 maximum

Physical Tests.

(*a*) Viscosity of GR-S—	
Mooney (large rotor) at 4 minutes	45 minimum to 55 maximum
(*b*) Viscosity of compounded stock—	
Mooney (large rotor) 212° F. at 4 minutes.	100 maximum
Mooney (small rotor) 212° F. at 4 minutes.	50 maximum
(*c*) Properties of vulcanizates, vulcanized 50 minutes at 292° F.	
Tensile strength, lb./sq. in.	2500 minimum
Elongation at break, per cent.	450 minimum
Modulus, 300 per cent. elongation, lb./sq. in.	800 minimum to 1400 maximum

METHODS OF ANALYSIS AND TEST.

Chemical.

(*a*) Acetone extract.
(*b*) Heat loss.
(*c*) Fatty acid.
(*d*) Soap.
(*e*) Ash.

Physical.

(*a*) *Mooney viscosity of GR-S.* The viscosity shall be determined on a Mooney viscometer with 1-minute warm-up at 212° F., reading at $1\frac{1}{2}$ and 4 minutes. The GR-S sample shall be aged at room temperature for at least 24 hours after baling before the viscosity determinations are made.

(*b*) *Mooney Viscosity of Compounded GR-S.* The viscosity of compounded stock, sampled as at operation 10 in the order of milling given

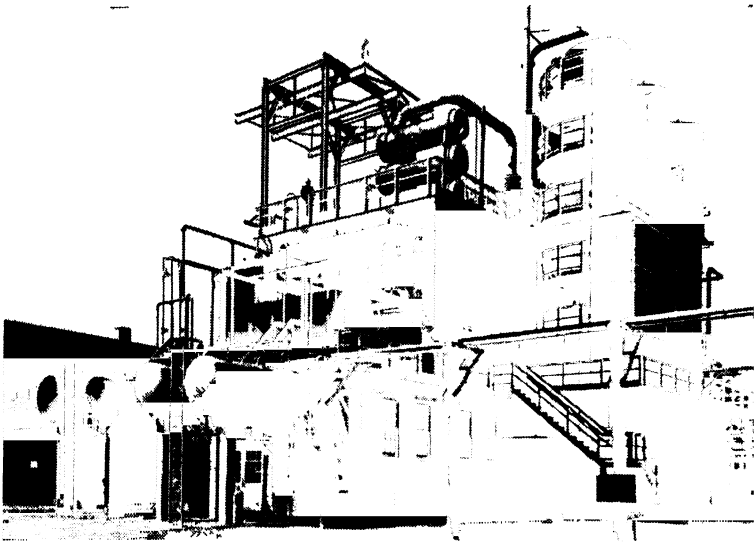


FIG. 60.—Recovery Building—Government-owned Plant built and operated by B. F. Goodrich Company.

below, shall be determined on a Mooney viscometer with a 1-minute warm-up at 212° F., using either a large or a small rotor, readings being taken at 4 minutes.

(*c*) *Properties of Vulcanizates.* The mixing formula is given as: GR-S (as received), 100; standard Wyex channel black, 50; B.R.T. No. 7, 5; zinc oxide, 5; sulphur, 2; mercaptobenzthiazole, 1·5. (Standard Wyex channel black is a coarse channel black, and B.R.T. No. 7 is a refined coal tar softener.)

All ingredients shall be weighed to within 0·25 per cent. of the weight specified, and the final weight of the mixed batch and the sum of the weights of all ingredients shall not differ by an amount exceeding 0·6 per cent.

Mixing of the rubber compound shall be done on a laboratory rubber mill with rolls 12 inches long by 6 inches outside diameter, with a working distance between the guides of 10½ inches. The speed of the slow roll shall be 24 r.p.m. and the gear ratio 1·4, or as near that figure as is compatible with good engineering practice. Sufficient cooling water shall be circulated through the mill rolls to maintain a roll temperature of 70° F.–100° F. at the start of the mixing and a maximum of 130° F. during mixing.

Order of Milling: (1) Two tight refinings of the crude rubber; (2) Adjust mill to proper opening to give continuous sheet on the mill; (3) Break down rubber for 10 minutes, making ten three-quarter cuts each way; (4) Add channel black slowly, cut two times each way, total time 10 minutes; (5) Add softener in one minute; (6) Add zinc oxide, accelerator, and sulphur in one minute; (7) Cut three three-quarter cuts each way; (8) Roll and pass the stock endwise through mill six times; (9) Sheet out—total time of mixing to this point, 28 minutes as a maximum—and allow to rest 8 hours; (10) Take viscosity specimen; (11) Refine by two passes through the tight mill, sheet to a thickness of 0·085 inch, and cure within 3 hours.

The curing temperature used is 292° F. ± 1° F. The mould is the standard mould recommended in A.S.T.M. D15–41, which gives slabs 6 inches by 0·075 inch.

Physical tests are carried out at 82° F.

Moisture Content of GR-S. The moisture content of natural rubber is not a matter of profound importance and has relatively little influence on behaviour. This is not so with GR-S.

Wiegand and Braendle [30] have established that the presence of moisture in GR-S has a profound influence on its behaviour. According to them:

1. Moisture content of uncured GR-S compounds must be reckoned with because of its effect on curing rate and the serious consequence of overcure.

2. Excessively dry polymer (below about 0·15 per cent. water) will, in general, be slow curing.

3. Mixed stock with less than 0·5 per cent. water will, in general, be slow curing and erratic in curing rate.

4. The normal moisture range of carbon black does not affect the curing rate of GR-S.

5. The normal moisture content of carbon black is not available to the polymer for stabilizing its curing rate.

6. Mixed stock which is dry and slow curing may be conditioned to stable curing rate by storage under humid conditions. A moisture

content of 0·5 to 1·0 per cent. is indicated. This moisture content seems also to iron out differences in curing rate between polymers.

7. Since conditioning of mixed stocks is not always feasible on the factory scale, the stabilization of cure by direct water addition during mixing should be given consideration.

8. Laboratory-scale tests on a GR-S tread compound indicate that an addition of about 2·5 to 5 per cent. water (on the polymer) during mixing will result in a mixed-stock moisture content giving minimal

FIG. 61.—Particles of Synthetic Rubber being separated from Water.

At lower left water containing the rubber particles flows down a trough on to a vibrating screen which is seen beneath the pipes. The white material here is synthetic rubber.

cure variation for normal-curing and slow-curing (very dry) polymers for periods of stock layover up to about 3 weeks.

9. Any additions of water as suggested above will, on the factory scale, require adjustment since moisture retention will be a function of the compounding ingredients, mixing cycle and temperature, storage time, and humidity conditions actually obtaining.

Processing of GR-S. The processing of GR-S, that is to say the conversion of GR-S into finished products, follows along the lines so well established for natural rubber. In fact, the large-scale production

of GR-S in the United States was decided upon because its general handling was nearest to that of natural rubber. The same plant is employed, similar compounding ingredients, much the same procedure is used and the difficulties encountered are not unlike. These conditions were absolutely essential for any large-scale usage in view of the scale and extent of the rubber industry. Otherwise progress would

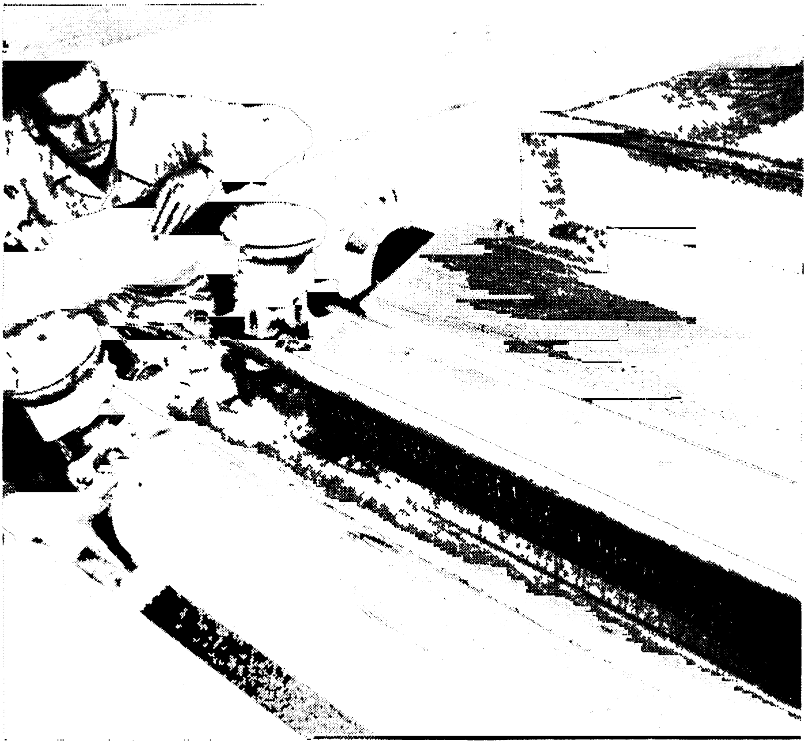


FIG. 62.—Washing and Filtering. After coagulation the synthetic rubber in the form of flocs or crumbs is washed and excess water is removed.

have been extremely slow. Standard GR-S is sufficiently like rubber that it has been used for at least 90 per cent. of all rubber applications.

So we find that GR-S has to be reduced to a plastic condition on mixing mills or internal mixes. Vulcanizing agents have to be added. Fillers and modifying agents must be incorporated in large quantities. Thereafter the plastic GR-S compound is extruded, or moulded, or otherwise processed prior to the final vulcanization process. Because of the fundamental differences between GR-S and natural rubber, there have been many difficulties. These have not yet been eliminated

completely. However, great progress has been made, so that at the present time vast quantities of GR-S are being used in rubber factories all over the world. The initial troubles and snags have been solved one after another.

And now the position is that almost any product which can be made with natural rubber can be reproduced in GR-S. Much remains to be done. But the early apparently insuperable difficulties have been overcome.

The softening of GR-S has been one of the most difficult factory problems. The structure of GR-S differs from that of natural rubber. When natural rubber is subjected to milling, i.e. treatment on the mixing rolls, there is a definite breaking-down process. The initial toughness or " nerve " is rapidly reduced and conversion to the plastic condition proceeds rapidly and smoothly. The softening of GR-S is quite different. GR-S is much tougher than rubber and much more effort is required to bring it to the plastic condition. The flow characteristics of the two materials are quite different.

The molecular structure is probably responsible for the difficulties. Raw rubber is considered to be a straight-chain polymer without any branching or cross-linking. GR-S seems to have a definite net-structure with plenty of cross-linkings. Until most of these cross-links are broken down there cannot be any marked plasticity developed.

Large-scale experience has shown that internal mixers are better suited than open mills for the mixing of GR-S. At quite an early stage in 1943, the No. 11 Banbury was recommended by the U.S. War Production Board as suitable. The conditions recommended were :

Speed	30 r.p.m.
Rotor clearance . . .	$\frac{3}{8}$ inch
Horse-power . . .	500

Other standard equipment lagged in capacity owing to the increased difficulties. Thus mixing capacities as compared with natural rubber were :

	%
60-inch mill	40
84-inch mill	60

According to Willshaw,[31] to give equivalent output power consumption increased by 20 per cent. Higher mixing temperatures were involved, which made handling of stocks much more difficult.

The softening of GR-S differs very greatly from the softening of natural rubber. It must be softened and its plasticity lowered in order that compounding may be carried out.

GR-S may be plasticized by hot or cold mastication by hot air treatment, or by passing it through a Gordon Plasticator. But until comparatively recently the "hot air" process was of great importance.

On the other hand, present-day grades of GR-S offer much less difficulty in processing.

Breakdown of GR-S. This breakdown of GR-S has been one of the greatest problems connected with its use. As it has had to be used in increasing quantities, so great resistance was developed among users accustomed to the relatively straightforward behaviour of natural

FIG 63—Flocs or Crumbs of Buna-S Synthetic Rubber travel on a Conveyor after being washed and pressed dry

rubber. Hardly any factory outside Germany was in a position to use the hot-air treatment. It is also a fact that GR-S is rather softer than the German Buna-S.

One of the clearest statements about the handling of GR-S has been given by Garvey, Whitlock and Freese.[8]

Synthetic rubber differs from natural rubber in several important respects. It is tougher and consequently tends to become hotter on the mill. Also it is shorter and less thermoplastic. These differences show up as a marked difference in milling behaviour. When crude natural rubber is put on a cold mill, it is tough and knotty until well

broken down. If the mill is heated to 180°–200° F., the rubber quickly smooths out, becomes soft, and is easily pulled out to a considerable extent. Under similar conditions the synthetic material smooths out somewhat more quickly on the cold mill, but remains rather tough and nervy. At 180°–200° F. it becomes considerably softer, but also becomes short and weak and is rougher than on a cold mill. Some of the experimental rubbers become so short and weak that they crack on the edges or become lacy, and in extreme cases fall off the mill.

With regard to oxidative or "heat" softening, GR-S synthetic rubber is intermediate between natural rubber and the oil-resistant butadiene copolymers. Under proper conditions it can be softened in hot air, but unless the conditions are carefully controlled, the operation may actually harden the synthetic rubber. This is due to the fact that the oxidation has a double effect, a breakdown and a sort of oxidation vulcanization or cyclization. In the first stages of heating, breakdown seems to be predominant and the rubber softens. Subsequently, however, the vulcanizing action becomes predominant and the rubber assumes a scorched appearance, becoming grainy, short, and hard.

The mill breakdown is probably related to the heat-softening action. The synthetic rubber does not break down so much as natural rubber does. Considerably more milling is necessary for adequate breakdown and the breakdown is less obvious. Nevertheless, it is important in subsequent operations. The breakdown can be carried through either before or after pigments are added. There is some indication that the addition of pigments facilitates breakdown. The important thing is that the overall milling must be adequate and that breakdown is favoured by a cool mill and a tight one.

Other Methods for Handling GR-S. Many other methods have been tried for softening GR-S. For example, it has been proposed to treat GR-S latex with small quantities of aromatic hydrazines such as phenylhydrazine, agitating for some hours and then passing oxygen through for 8 hours. Thereafter the latex is coagulated.

Numerous proprietary materials have become available which aid the thermal softening or processing of GR-S. These peptizers include arylhydrazines, phenylhydrazine, benzaldehyde, phenylhydrazone, and some aromatic mercaptans. Furfural phenylhydrazone is said to be very effective. Iron naphthenate is also useful. Nitroso-β-naphthol has also found some use in plasticizing GR-S during hot mastication.

Although oxygen is absolutely essential to plasticize the material successfully, yet the amount of oxygen taken up is too small to be

measured. The plasticized Buna-S tends to revert to its original condition if left for any length of time. It is interesting to note that the acetone extract of Buna-S is between 6 and 7·5 per cent.

The situation with regard to premastication of GR-S has greatly changed. In fact, in most cases premastication is no longer carried

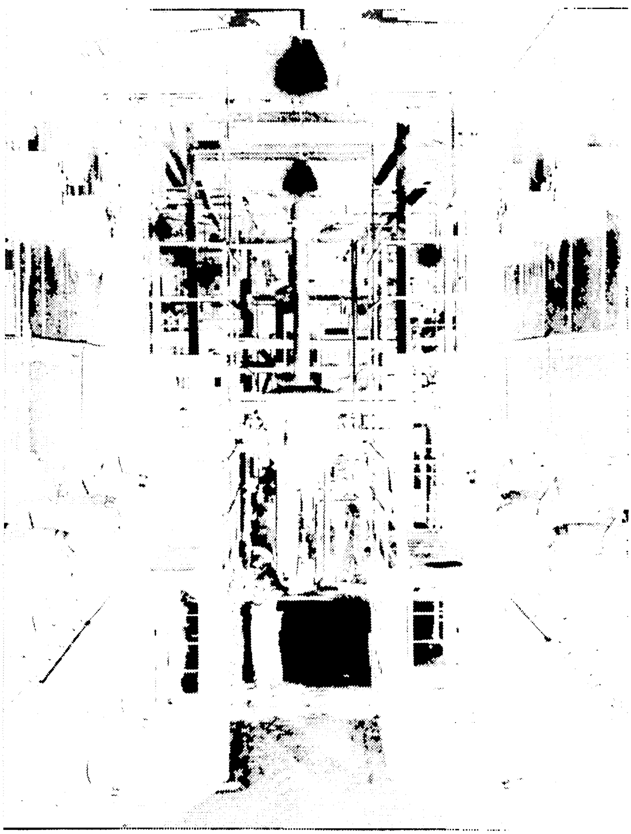


FIG. 64.—Drying.

GR-S synthetic rubber is dried by passing back and forth three times in twelve enormous driers at the Institute Plant. At full operation these driers will evaporate 160 tons of water per day.

out. It has been superseded by a first-stage mixing process including much of the carbon black.

Once plasticized, there is no further difficulty in processing. Thereafter, the handling follows ordinary rubber practice. One of the outstanding points about Buna-S is that when compounded without fillers, i.e. as a pure gum mix, the physical properties are incomparably inferior to those of natural rubber. Reinforcing fillers, notably carbon

black, are essential to show them at their best. Fillers of all types may be incorporated according to the product being made. Sulphur and accelerators have to be added to effect vulcanization. Higher amounts of plasticizers are used than in ordinary rubber practice. In order to bring out the best physical properties, high proportions of reinforcing carbon blacks are generally added. Conditions of vulcanization and general handling are parallel to standard rubber technique. The material may be calendered or extruded; it may be moulded, etc.

Thermal softening does not appreciably enhance tackiness, which has consequently to be developed by other methods. In actual practice this has been attained by the use of small amounts of:

(*a*) rubber,
(*b*) reclaim,
(*c*) softeners such as coal-tar derivatives, or petroleum residues.

Almost the greatest disadvantage of GR-S is the lack of tack, in which property it is far inferior to rubber. This complicates the processing of many articles.

The tear resistance of GR-S products is invariably inferior to that of corresponding rubber articles.

The property of tackiness is of fundamental importance in the fabrication of multicomponent products, such as tyres and belts. No generally acceptable quantitative measurement has yet been evolved for its evaluation. Tackiness should be distinguished from stickiness. Juve [11] has defined tackiness as

> that property of a rubber or compounded stock which causes two layers of stock, which have been pressed together, to adhere so firmly that separation under force will occur at some point other than at the original two surfaces. If tearing such as this occurs, tackiness is rated as excellent. If no tearing occurs, tackiness is rated as poor, while if some tendency to tear is observed the rating may be good or fair, depending on the degree of tearing. Stickiness, on the other hand, results in separation at the surfaces attached, but the separation may take place with varying degrees of force. Based on this differentiation between tackiness and stickiness, natural rubber is rated as having excellent tackiness, GR-M and GR-I fair tackiness, and GR-S none. Compounding techniques modify these ratings, in some cases reducing tackiness and in others increasing it. However, it has not yet been possible to attain any considerable degree of true tackiness in GR-S.

Almost the chief practical difficulty with GR-S has been this lack of tackiness. The degree of tackiness attained with GR-S is so small compared with the tack of natural rubber. It is serious because many leading fabrication processes depend on precisely this feature. Recourse is often had to the use of rubber cements.

In particular one may mention difficulties such as:

(1) Lack of adhesion between plies in moulded articles.

(2) The inability to ply-up frictioned or spread fabrics. Thus in tyre building there is a lack of tackiness in calendered fabric. It is necessary to apply a varnishing coat of rubber solution to give the essential "building tack".

(3) The failure to make satisfactory laps and joints in articles.

(4) Necessity to incorporate large amounts of softeners which lead to processing troubles.

FIG. 65—Strip of Synthetic Rubber as it comes off Sheeting Mill

Influence of Rubber. The best method of alleviating the processing difficulties with GR-S is by addition of either rubber or whole-tyre reclaim.

These additions undoubtedly facilitate processing. They contribute their own inherent tack to the resulting material. As a consequence, most production based on GR-S has until recently relied on the addition of up to 20 per cent. of rubber or of reclaim to overcome the chief snags.

Prettyman[22] has investigated the influence of additions of rubber and reached the following conclusions:

1. The addition of a small amount of natural rubber to a GR-S tread stock (say 10 per cent.) appreciably increases flex-cracking life. Conversely, the addition of a similar amount of GR-S to a rubber tread stock decreases cracking life.

2. Similar results may be anticipated where guayule is substituted for rubber, or reclaim for GR-S.

3. Reclaim and GR-S may be blended in any proportion with relatively little change in flex-cracking resistance. Some superiority in the case of high-percentage reclaim stocks is indicated.

4. The order which might be anticipated for cracking of tyres made from the single polymer stocks studied, in order of decreasing merit, is: natural rubber, guayule, reclaim and GR-S, with little choice between the latter two.

As part of an exceptionally fine study of synthetic rubber behaviour, Drogin[6] has prepared Buna-S mixes containing 20 parts of rubber and reclaim respectively to 80 parts of Buna-S. His Buna-S was the material available in the United States prior to the official designation of GR-S. His results are summarized in Tables 91 and 92.

Addition of rubber improves all characteristics, and particularly

TABLE 91. FORMULATION—SMOKED SHEET OR RECLAIM IN SYNTHETIC RUBBER

	Buna-S	Blend of Buna-S	
		Smoked sheet	Reclaim
Buna-S	100	80	80
Smoked sheet	—	20	—
Whole tyre reclaim	—	—	20
Zinc oxide	5	5	4·5
Stearic acid	1	2	1·8
Pine tar	3	3	2·75
Paraflux	3	3	2·75
Altax	1·25	1·25	1·1
Sulphur	2	2·3	1·97
Kosmobile 77	50	50	43·4
	165·25	166·55	158·27
Press cure	292° F.	292° F.	292° F.

TABLE 92. DETAILED TEST DATA—SMOKED SHEET OR RECLAIM IN SYNTHETIC RUBBER

	Buna-S	Buna-S and smoked sheet	Buna-S and reclaim
Plasticity (mm.)	364	335	357
Extrusion (seconds)	5·8	4·0	5·1
Modulus at 300%	800	1675	1340
Tensile strength	2590	2710	2050
Elongation at break	620	545	425
Shore hardness	60	65	69
Tear resistance	540	508	524
Abrasion resistance	277	158	238
Percentage rebound	37	37	37
Heat build up—			
Average temp. ° F.	204°	180°	183°
Percentage compression	10·6	6·1	7·9
Percentage set	9 6	4·0	6·0
Electrical resistance	8×10^9	2×10^9	17×10^9

processing. With reclaim, only the tensile strength is less, otherwise all properties are improved. Table 93 illustrates this.

The Use of Reclaim. The Vanderbilt Company [24] tried out compositions of Buna-S containing reclaimed rubber. Reclaim helped the processing considerably, but reduced the physical properties more than a comparable load of reclaim on natural rubber.

TABLE 93. COMPARATIVE RECLAIM MIXFS

	A 1	A 2	A 3	B 1	B 2	B 3
Smoked Sheet	75	50	25			
Buna-S	—	—	—	75	50	25
Whole-tyre reclaim	50	100	150	50	100	150
Reogen	2	2	2			
Stearic acid	3	3	3			
Pine tar	1	1	1			
Agerite resin D	1	1	1			
Agerite hipar	1	1	1			
Zinc oxide	3	3	3	3	3	3
Sulphur	3	3	3	2	2	2
Captax	1	1	1	—	—	—
Altax	—	—	—	1·5	1·5	1·5
Channel black	50	50	50	50	50	50

They made up three equivalent combinations of whole-tyre reclaim with Buna-S, and with smoked sheets. A mix containing 50 parts of Buna-S and 100 parts of whole-tyre reclaim gave tensile properties almost equal to another mix containing 75 parts of Buna-S and 50 parts of reclaim. The use of the first mix would therefore represent a considerable saving in Buna-S with very little loss of tensile properties. Ample tack was produced in these mixes by the use of 3 per cent. to

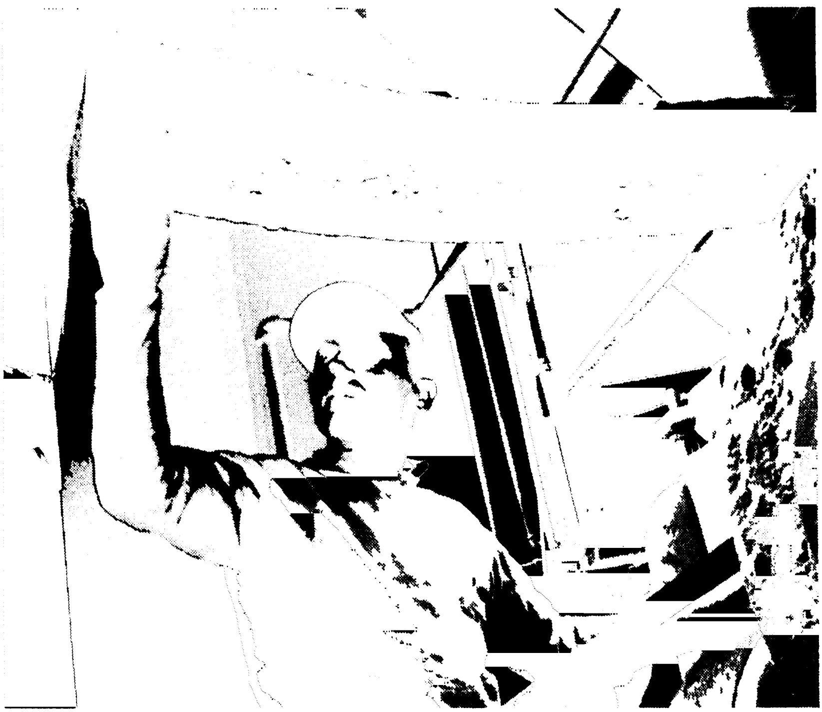


FIG. 66—Finished GR-S comes off a Final Mill in a Continuous Ribbon.

5 per cent. of Reogen (a mixture of mineral oil, sulphonated petroleum oil, and normal butyl alcohol) on the reclaim. Although Reogen is not a tack producer for Buna-S, it does act on the reclaim and provides tack for the combination. With this 50 Buna-S—100 reclaim mix, the comparative effect of four fillers, channel black, soft gas blacks (P33 and Thermax), and finely divided calcium carbonate (Kalvan) was determined. Although channel black gave the best overall results, greater loadings of the soft blacks gave some physical properties such as resilience and adhesion to steel that were better.

TABLE 94. PROPERTIES OF BUNA-S—RECLAIM COMBINATIONS [20]

	M_{300}	T_B	E_B	Aged 48 hours in oxygen bomb at 300 lbs. and 80° C.			Impact resilience	H	Permanent set percentage	Compression set percentage
				M_{300}	T_B	E_B				
A_1	1370	3300	570	1635	2470	460	34	70	40	21·1
A_2	1350	2560	515	1565	2110	410	31·5	71	45	18·1
A_3	1300	1930	450	1425	1585	365	30·5	70	40	20·8
B_1	1275	1980	440	1685	2080	375	35	64	15	24·5
B_2	1430	1925	400	1485	1865	400	32	66	20	21·7
B_3	1170	1520	405	1315	1560	375	30	64	20	25·6
	15 min. cure at 290° F.						20 min. cure			20 min. cure

TABLE 95. BUNA-S AND RECLAIM MIXES [20]

	B 2	B 4	B 5	B 6
Buna-S	50	50	50	50
Whole-tyre reclaim	100	100	100	100
Agerite resin D	2	2	2	2
Zinc oxide	3	3	3	3
Sulphur	2	2	2	2
Altax	1·5	1·5	1·5	1·5
Channel black	50	—	—	—
P 33	—	60	—	—
Thermax	—	—	60	—
Kalvan	—	—	—	100

TABLE 96. TENSILE PROPERTIES OF BUNA-S—RECLAIM MIXES [20]

	M	T_B	E_B	Aged 48 hours in oxygen bomb at 300 lbs. and 80° C.			Impact resilience	H	Permanent set	Compression set
				M	T_B	E_B				
B 2	1430	1925	400	1485	1865	400	32	66	20	21·7
B 4	660	1300	525	725	1140	505	39	52	22	21·3
B 5	765	1250	490	820	955	380	44	51	20·5	24·2
B 6	465	1180	550	570	955	510	33·5	53	26	32·7
	15 min. cures at 290° F.						20 min. cure			20 min. cure

Compounding of GR-S. In conformity with the manufacture of rubber goods this implies the addition of:

1. Sulphur or suitable vulcanizing agent.
2. Accelerators and anti-oxidants.
3. Fillers and modifying agents.

Willshaw [31] has shown some of the problems associated with tyre manufacture. A typical process involves up to five stages of mixing with delays of at least 12 hours between first and second and delays of 8 hours subsequently.

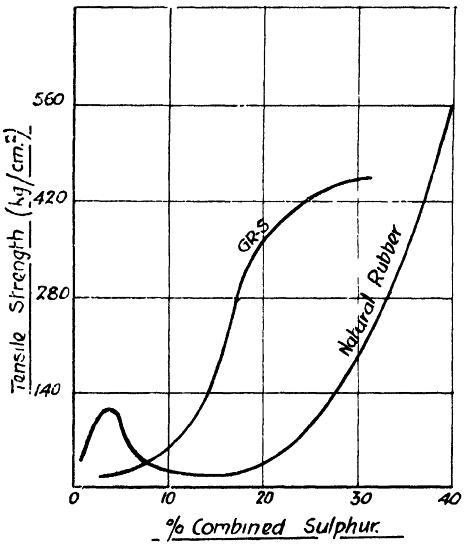


FIG. 67.—Tensile Strength with Varying Combined Sulphur.

Sulphur is the chief vulcanizing agent employed in GR-S products. There are other minor materials employed for special purposes, but sulphur predominates.

Sulphur is soluble in GR-S, and when present enables it to be vulcanized by heat. Vila and Holbrook [29] have found that below 55° C. sulphur is less soluble in GR-S than in rubber, but above that temperature it is more soluble. Sulphur mixes readily into softened GR-S and presents no problem.

No satisfactory method has been evolved to assess the degree of cure and the optimum cure of GR-S. The usual methods used for rubber based on tensile strength and elongation at break are only of limited value in assessing cure.

GR-S shows no tendency to revert on overcure and shows fewer signs of overcure than does natural rubber. "*Reversion*" is when the vulcanized rubber becomes tacky, soft and loses elasticity. The general tendency is to judge the cure on modulus values and to select as the optimum the point at which the modulus-time of cure curve flattens.

There is as yet no single simple method of judging optimum cure, and therefore in deciding the cure it is best to consider the specific function of each type of article.

Rigid adherence to the methods found satisfactory with natural rubber stocks is not satisfactory.

Cheyney and Robinson [4] have examined the behaviour of straight GR-S sulphur mixtures. GR-S was mixed with various quantities of sulphur and vulcanized. They determined "free" and combined sulphur. They also examined the physical properties of the vulcanized materials. These pure-gum mixes have low values for ultimate tensile strength and for elongation. In the soft rubber region, maximum tensile strength was obtained at 6 per cent. sulphur content. Hard rubbers were formed with approximately the same sulphur content as in hard natural rubber.

Bruce, Lyle, and Blake [2] have studied the heat of vulcanization of GR-S compounds. They concluded that:

(*a*) The heats of vulcanization for natural rubber and GR-S are nearly equal. The data for both materials indicate two different chemical reactions during vulcanization. At low sulphur percentages the principal reaction forms soft vulcanized rubber and is accompanied by little or no heat evolution. Above the 2 per cent. sulphur region, a second reaction predominates, forming hard rubber and producing a relatively large quantity of heat.

(*b*) The presence of an accelerator (Santocure) in GR-S has little, if any, effect on heat of vulcanization.

(*c*) The addition of carbon black to GR-S lowers the heat of vulcanization in the region above 4 per cent. sulphur. The calories evolved in a 10 per cent. sulphur compound decrease linearly with percentage of carbon black.

Morris, Mitton, Seegman, and Werkenthin [18] have made a survey of hard GR-S with regard to sulphur requirement and effects of various pigments, softeners, and accelerators on tensile strength, ultimate elongation, hardness, and stiffness. Of particular interest were the observations that hard GR-S had a higher tensile strength than hard Hevea rubber, and that hard GR-S did not undergo much loss in tensile

strength when compounded with 60 volumes of channel black or semi-reinforcing black.

Kemp, Ingmanson, Howard and Wallder [13] find that the temperature coefficient is 2·07 per 10° C., which is within the range of a first-order chemical reaction.

The available evidence relating to vulcanization of GR-S may be summarized as follows:

1. Sulphur is the chief vulcanizing agent employed.
2. Vulcanization is much slower than with rubber.
3. The amount used is lower than is customary with natural rubber.

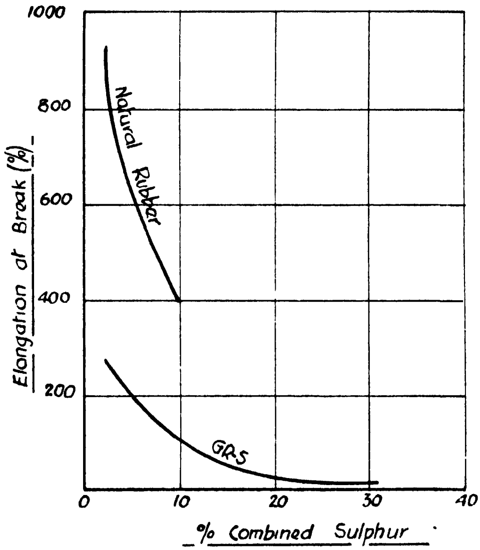


FIG. 68.—Elongation with Increasing Combined Sulphur.

4. Accelerators are not so effective as with rubber.
5. More accelerator is required.
6. High sulphur content improves resilience and hardness.
7. High sulphur content decreases tear resistance and cutting resistance.
8. High sulphur content tends to accelerate hardening after ageing.
9. The most widely used materials are based on 2 parts sulphur per 100 parts GR-S.

Accelerators. GR-S does not vulcanize as rapidly as natural rubber. As in the case of natural rubber, accelerators exercise a profound influence in the speed of vulcanization and on the properties of

the " cured " product. They are of even greater importance for GR-S because it is slower curing in itself than is rubber. The metallic oxides—litharge, magnesia, zinc oxide, etc.—accelerate the vulcanization of GR-S as they do rubber. Nearly all the standard accelerators are effective with GR-S. Their behaviour in GR-S is not parallel to the behaviour in corresponding rubber compounds. To give a single example, whereas diphenyl guanidine is effective in rubber mixes, it seems to be indifferent in GR-S. Consequently the behaviour of accelerators in GR-S has been the subject of considerable study.

FIG 69.—GR-S Synthetic Rubber is pressed into a Loaf 18 × 28 × 6 inches. Each loaf weighs 75 lbs, and at full operation the Institute Plant turns out 9,000 such loaves per day

In general, it requires less sulphur and more accelerator. Most organic accelerators serve to speed up the GR-S sulphur cure. Thiazoles and activated thiazoles are very effective. On the other hand, diphenyl guanidine is ineffective. As in the case of rubber, ultra accelerators such as thiuram-disulphides can be used for low-sulphur cures. The thiuram-monosulphides have also proved extremely useful. There is little tendency towards scorching while they give flat-curing characteristics, i.e. there is reduced tendency towards overcure. Some of the aldehyde-amines show promise, such as butyraldehyde-amine.

The Germans used Vulkacit AZ extensively. It is the product obtained by reacting equimolecular proportions of diethylamine and mercaptobenzthiazole. It is admirably suited to the GR-S type of material, giving high tensile strength, good elongation, good ageing. It is very flat curing with a pronounced plateau effect.

Another very effective specific accelerator is cyclohexyl benzthiazyl sulphenamide, known as Santocure. It gives stocks having high resilience and low heat build-up.

TABLE 97. EFFECT OF VARYING AMOUNTS OF SULPHUR ON PHYSICAL PROPERTIES

(Curing period: 20 min. Temp.: 141° C.)

GR-S	100
Carbon black	50
Zinc oxide	3
Coal-tar softener	5
Benzothiazyl disulphide	1·0
Litharge	1·5
Sulphur	variable

% Sulphur	Tensile strength	% Elongation	Modulus at 300% elongation
0·75	3840	670	980
1·0	4000	665	1120
1·5	3600	665	1190
2·0	3620	670	1025
	After Ageing 24 Hours at 100° C.		
0·75	3460	610	1240
1·0	3380	530	1510
1·5	3000	400	2080
2·0	2770	340	2280

The Use of Metal Oxides. As is the case with natural rubber, certain metal oxides accelerate the vulcanization of GR-S with sulphur. Litharge and magnesia give faster cures than zinc oxide, but zinc oxide is the best activator in the presence of acidic accelerators. When used solely as an activator, there is evidence that maximum tensile strength and modulus are obtained with 1·25 parts of zinc oxide per 100 parts of GR-S, but that a minimum of 4·5 parts is necessary to confer maximum resistance to ageing.

Litharge has been found to be particularly effective used together with benzothiazyl disulphide. The combination used with low sulphur gives good heat stability. The modulus is maintained high and steady, while brittleness is minimized and tear resistance is definitely improved.

GR-S contains 3–6 per cent. of fatty acids (calculated as stearic acid). As a result, only small quantities are added in compounding.

Vila [28] considered that dithiocarbamates are satisfactory accelerators offering ready means to offset the slow vulcanization of GR-S.

Accelerator behaviour may be summarized as follows:

1. Best all-round accelerators are dibenzthiazyl disulphide and mercaptobenzthiazole.
2. Best fast accelerators are thiuram disulphides.
3. Dithiocarbamates are very effective.
4. These two latter types are effective boosting accelerators for the thiazoles.
5. Diphenyl guanidine is ineffective.
6. Aldehyde-amine accelerators can be employed.

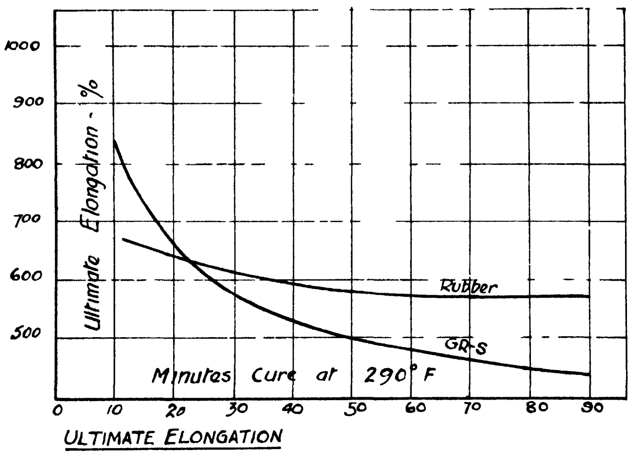


FIG. 70.—Elongation at Different Cures

In the production of GR-S ebonites, ultra-accelerators of the thiuram disulphide class are very effective. Thus, using a mix GR-S 100; ebonite dust 30; sulphur 35; zinc oxide 5; vulcanization could be carried through as follows:

Tetramethylthiuram disulphide	Vulcanizing period at 160° C.
–	2 hours
1	1 hour
5	30 minutes
–	2 hours
1	45 minutes
5	15 minutes

Some success has been attained in the vulcanization of GR-S compositions at low temperature. As GR-S cures more slowly than rubber, more powerful accelerators are involved. The technical importance of low-temperature cure arises chiefly in connection with proofed goods. There is also the important field of dipped articles, while cements are of considerable significance. The straightforward cold-curing of GR-S with sulphur chloride is practicable, but is not as successful as with rubber.

FIG. 71—Folding Synthetic Rubber into Bales in Finishing Line Conveyor.

Accelerators such as Butyl 8 and Robac Gamma enable vulcanization to be carried out at room temperatures, although the times taken are longer than with rubber stocks. Thus periods of 3 days are necessary with 3 parts Butyl 8 and 2 parts sulphur in pure gum GR-S.

Macpherson has described how GR-S can be vulcanized by treatment with H_2S and SO_2—the Peachey Process.

Ageing of GR-S. The ageing of GR-S in comparison with rubber has become a somewhat confusing subject. This is due to the fact that there are several aspects to ageing. In some, GR-S is superior to rubber; in others, it is very inferior.

GR-S gives a vulcanized material much more resistant to deterioration by oxidation than does rubber. However, there are two serious shortcomings of GR-S, namely, the poor resilience and the property of hardening up if exposed to heat. The poor resistance leads to high hysteresis which builds up excessive heat under severe stresses. This in turn clearly aggravates the hardening up. The subject of heat embrittlement has been widely studied owing to the fact that these effects become pronounced in GR-S inner tubes and tyres. They are the important factors involved in the premature failure of GR-S articles under service conditions in the past. In general, the effect of heat tends to give a shorter, more brittle stock, becoming harder and with a higher modulus. The elongation decreases, as do tensile strength and tear resistance. According to Massie and Warner [16], the rate of deterioration of these characteristics approximately doubles for each 10-degree rise in ageing temperature. The behaviour of natural rubber is in sharp contrast to this, because when subjected to continuous heat it usually becomes softer, depolymerizes, or reverts.

The heat ageing of natural rubber is regarded as a combined effect of depolymerization, oxidation and after-vulcanization. In rubber the degree of deterioration usually depends on the amount of sulphur present, the type of accelerator, and the use of antioxidants.

It seems likely that GR-S articles subjected to heat ageing deteriorate by the combined action of several influences. Among these may be cited :

(*a*) The instability of the GR-S polymer itself.
(*b*) There may be some action of carbon black on GR-S.
(*c*) Small amounts of sulphur or sulphur compounds in polymer and softener may have some influence.

Massie and Warner point out that such a mixture does change extensively, even without further additions of curing agents. They suggest that hysteresis and heat build-up are generally dependent on the state of cure.

Shelton and Winn [25] noticed that the hardening effect observed on heating GR-S vulcanizates in a bomb at 80° C. was independent of the presence of oxygen and took place to an equal extent in the presence of nitrogen. On ageing at 100° C., however, they observed that more than half the increase in modulus on heating could be attributed to the presence of oxygen.

The conclusions of Sturgis, Baum and Vincent [26] are at variance with this latter result, since they reported that there was much hardening on heating the vulcanizates in nitrogen at 100° C. as with oxygen.

They observed further that the effect of accelerator activity on heat stability (i.e. heat embrittlement resistance) was very slight and that the effect of sulphur content was noticeable but not large. Nevertheless, they concluded that the system GR-S sulphur was inherently unstable and recommended sulphurless vulcanization, using dinitrobenzene as the vulcanizing agent. Neal and Ottenhoff[16], using exclusively MBT-DPG acceleration, claimed that high accelerator and low sulphur content tends to give good heat stability in GR-S vulcanizates.

Massie and Warner have observed that so-called "persistent" accelerators, e.g. mercaptobenzthiazole, give a modulus which steadily increases with time of cure, while "non-persistent", e.g. dithiocarbamate, accelerators minimize this effect. Low-sulphur formulations show better heat stability than more conventional stocks. Juve and Garvey [12] have shown that the rate of sulphur combination with GR-S under vulcanizing conditions is faster and more complete with tetramethyl thiuram monosulphide than with MBT-DPG acceleration. They suggest that such "flat-curing" accelerators, because they promote more rapid and complete sulphur combination, do not leave so much free sulphur to cause embrittlement on heating. They found that with tetramethyl thiuram monosulphide over-cured products gave better heat stability than under-cured products.

Hendricks [10] pointed out that a compound designed to give good heat build-up, i.e. a compound with fairly high proportions of sulphur and accelerator, tends to show poor heat stability, while a compound with low sulphur content, designed to give good heat stability, tends to give high heat build-up on stressing. He suggests that the most satisfactory compromise, to get satisfactory heat stability and heat build-up, comes from vulcanizing GR-S with a minimum of sulphur "driven home" by a powerful and active accelerator combination. In the course of this paper Hendricks points out that with certain commonly used accelerators in GR-S, while there is in general a decrease in ultimate elongation with the increase in time of cure, after ageing in the air oven there is actually in some cases an increase in elongation with time of cure. The heat stability is therefore better at over-cures.

Softeners for GR-S. Owing to the lack of tack in GR-S, and the difficulty of inducing this characteristic during processing, it is essential to add softeners and plasticizers to obtain these effects. The most effective materials added in this respect are rubber and iron naphthenate. Many other softeners are added which aid processing without giving any substantial or durable tackiness. Among these may be mentioned aromatic petroleum distillates, coal-tar extracts, bitumens, coumarone resins. Reclaimed rubber is another material which is

added in order to achieve these objects. The addition of these materials in general do not improve tensile strength, but they tend to improve the elongation and tear strength.

Compounds of great softness and high strength are not possible with GR-S because of the poor quality of non-reinforced stock and the high nerve of lightly pigmented material. Soft GR-S stocks are made by reinforcing fully and then adding softeners, a procedure which tends to give materials showing too much flow.

Pure gum GR-S compounds are so poor in physical properties that reinforcing agents must be added.

Carbon-black fillers are pre-eminent for GR-S. Apart from tyre treads, most GR-S articles contain more carbon black than do their natural-rubber counterparts. Latterly there has been a trend towards the use of special white fillers in association with carbon black. The types of blacks chiefly used are the furnace blacks. These are a relatively new class, the production of which has been expanded tremendously to meet the requirements for GR-S. The technique adopted for the incorporation of the blacks varies to some extent. It is extremely important because the reinforcement obtained depends very greatly on the degree of dispersion of the filler, and carbon black is a difficult filler to disperse. The most favoured procedure appears to be the preparation of a master batch of GR-S with carbon black, as the first stage of mixing. The preferred method of doing this is in internal mixers. In some cases the addition of the black in several successive portions is adopted. However, in the tyre-tread class of material the GR-S and carbon black are mixed for about 35 minutes, the material being thereafter sheeted out between close rolls and allowed to stand for a period up to 24 hours. It is then broken down again on mixing rolls and the remaining ingredients are added. The addition of these other ingredients does not present any difficulties. Sulphur is added at the final stage in the normal way.

GR-S Properties Compared with Rubber. Drogin [6] compared a number of types of GR-S with smoked sheet for such properties as elasticity, tensile strength, modulus, elongation, hardness, tear resistance, and so on. There were marked differences in the materials. He compared them in pure gum mixes, that is, without any filler loading, and then proceeded to study the influence of different types of carbon black at various loadings. His main object was to evaluate the influence of different types of carbon black, the hard reinforcing channel blacks, the softer semi-reinforcing materials, the soft non-reinforcing blacks and so on. His results gave a very excellent picture of the best type of carbon blacks to use for any specific purpose. He showed quite clearly

the importance—in fact the absolute necessity—of using a black filler in order to obtain the best characteristics with the elastomer. For example, he found that the best loading of reinforcing carbon black

TABLE 98. COMPOUNDS EMPLOYED [6]

	Pure gum		Reinforcing black		Semi-reinforcing black	
	Rubber	Buna-S	Rubber	Buna-S	Rubber	Buna-S
Elastic	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	3.5	1.5	2	1.5
Altax	1	1	1	1.25	0.65	1.25
Pine tar	—	-	3	3	—	1.5
Paraflux	—	—	—	3	—	1.5
Sulphur	2	2	2.85	2	2.85	2
Dixie 20/Kosmos 20	—	—	—	—	60	60
Kosmobile 77 Dixiedensed 77	—	—	50	50	—	—

Press cured to optimum tensile values at 292 F

TABLE 99 COMPARISON OF MIXES CONTAINING CARBON BLACKS [6]
(Natural Rubber Properties rated as 100 in each case)

	Pure gum					Reinforcing black					Semi-reinforcing black				
	Smoked sheet	A	B	C	D	Smoked sheet	A	B	C	D	Smoked sheet	A	B	C	D
Plasticity	100	56	51	40	59	100	80	66	58	86	100	48	44	34	42
Extension	100		—	—	-	100	36	39	16	32	100	33	45	19	25
Modulus	100	—	—	—	—	100	59	55	83	62	100	63	66	92	60
Tensile	100	15	13	21	11	100	74	64	73	74	100	80	56	78	78
Elongation	100	74	55	78	52	100	121	110	102	120	100	124	116	95	122
Hardness	100	74	89	100	100	100	94	94	97	94	100	94	92	100	92
Tear	100	17	15	37	9	100	33	40	27	27	100	48	47	37	43
Abrasion	100	—	—	—	—	100	87	73	151	115	100	87	78	105	85
Rebound	100	74	78	85	81	100	88	77	90	90	100	91	79	91	91
Heat build-up %	—	—	—	—	—	—	59	67	44	58	—	53	42	51	42

A Naugatuck Buna-S B - Buton-S. C - Chemigum IV D = Hycar TT.

such as Kosmobile 77 was 50 parts per 100 of elastomer; whereas in rubber the best results are obtained at about 40 parts carbon black. It is of interest to observe the difference in the rubber composition and the Buna-S composition required to give balanced comparable materials.

TABLE 100. SIX DIFFERENT BLACKS IN BUNA [6]

(50 parts per 100 Buna-S)

	Kosmobile-S Dixiedensed-S	Kosmobile 77 Dixiedensed 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20	P 33	Thermax
Plasticity (mm.)	404	380	360	307	277	270
Extrusion (seconds)	15·5	11·6	4·9	3·3	3·0	3·1
Modulus at 400%	1300	880	1095	1530	625	490
Tensile strength	3250	2780	2600	1915	1700	1575
Elongation at break	475	615	525	475	720	890
Shore hardness	65	63	60	56	51	48
Tear resistance	408	331	349	200	164	145
Abrasion resistance	197	163	224	223	522	765
Percentage rebound	38	40	45	50	50	53
Heat build-up :						
Average temp. F.	181	190	189°	165°	160°	190°
Percentage compression	6·0	8·1	6·6	3·8	4·2	9·2
Percentage set	4·0	6·4	6·0	4·0	6·0	10·0
Percentage shrinkage	4·3	6·7	4·8	11·5	11·0	10·6
Electrical resistance	$1{\cdot}9 \times 10^6$	13×10^8	$10{\cdot}4 \times 10^6$	34×10^8	35×10^8	34×10^8
Process of manufacture	Channel	Channel	Special furnace	Furnace	Furnace	Furnace
Type	Hard	Soft	Reinforcing	Semi-reinforcing	Soft	Very soft

TABLE 101. FORMULATION—BUNA-S TREAD COMPOUND [6]

	Dixiedensed 77 Kosmobile 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20
Buton-S	100	100	100
Zinc oxide	5	5	5
Stearic acid	2·5	2·5	2·5
Pine tar	1·3	1·3	1·3
Wool grease	2·4	2·4	2·4
Bardol	2·4	2·4	2·4
Agerite powder	0·8	0·8	0·8
Sunproof	1·7	1·7	1·7
Santocure	1·4	1·4	1·4
Sulphur	1·8	1·8	1·8
Black	50	55	60
	169·3	174·3	179·3
Press cure	280° F.	280° F.	280° F.

With semi-reinforcing carbon black such as Kosmos 20 Drogin found an addition of 60 parts on the 100 to be most suitable both for rubber and Buna-S. So far as the softer carbon blacks, such as P 33 and Thermax are concerned, these gave much lower reinforcement of the Buna-S. On the other hand, they process more easily and larger

TABLE 102. DETAILED TEST DATA—BUNA-S TREAD COMPOUND [6]

	Dixiedensed 77 Kosmobile 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20
Black loadings	50	55	60
Plasticity (mm.) [a]	362	318	260
Extrusion, seconds [b]	2·4	1·7	1·4
Modulus at 300% [c]	1100	1625	1200
Tensile strength (maximum) [c]	2215	2080	1615
Elongation at break [c]	460	360	370
Shore hardness [c]	61	60	55
Percentage tensile depreciation [d]	12	4	35
Tear resistance [c e]	545	282	242
Abrasion resistance [c f]	162	100	168
Percentage rebound [c g]	39	42	45
Percentage shrinkage [h]	6·3	4·8	9·6
Flex resistance, flexes [i]			
Incipient cracking	405	1275	405
Deep cracking	1550	2525	1050
Final break	2210	3380	1150
Heat build-up [c k]			
Average temp. ° F. [l]	175°	166°	161°
Percentage compression	6·2	2·5	1·3
Percentage set	6·0	3·2	3·2
Electrical resistance [m]	$3{\cdot}2 \times 10^8$	$1{\cdot}6 \times 10^5$	$6{\cdot}8 \times 10^8$

[a] Williams plastometer, at 70° C.
[b] Firestone-Dillon plastometer, 15 lbs. pressure.
[c] For cure which produced maximum tensile strength.
[d] Aged 24 hrs. in oxygen bomb at 80° C. and 300 lbs. oxygen pressure.
[e] Winkelmann test, crescent-shaped piece.
[f] Grasseli abrader. [g] Lupke-type machine.
[h] Shrinkage of a standard dumbell test piece.
[i] De Mattia machine, stroke 3-inch, r.p.m. 300.
[k] Goodrich flexometer, stroke 0·150-inch, load 147·5 lbs., r.p.m. 1800.
[l] Average of 30-minute cycle.
[m] Measured with Volt Ohmyst Jr., calculated to ohms-cm.[3]

amounts could be added. The cure is much more rapid. The tensile strength obtained is about the same and the heat build-up is lower. The resilience of these compounds is also rather improved.

Drogin also tried the behaviour of 60 parts lampblack and acetylene black in natural rubber and Buna-S rubbers. He found lampblack to have effects somewhat similar to those shown by semi-reinforcing

black, e.g. Kosmos 20. Acetylene black behaved in a manner between this and the reinforcing hard black, e.g. Kosmobile 77. Acetylene black showed a much higher heat build-up. The conductance was outstandingly good, which indicates its application for conducting synthetic rubbers, parallel to conducting rubber.

The most important fact brought out by Drogin was that the best type of black to use was a specially prepared furnace black. In this case Kosmos 40 is of the reinforcing type, approaching hard reinforcing channel black in reinforcement, but much easier to process. It is faster curing, has higher modulus, better resilience, and lower heat build-up than channel black.

TABLE 103. SUMMARY OF TEST DATA—BUNA-S TREAD COMPOUND [6]

	Dixiedensed 77 Kosmobile 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20
Black loadings	50	55	60
Plasticity	100	114	139
Extrusion	100	141	171
Modulus	100	148	109
Tensile	100	94	73
Elongation	100	78	80
Hardness	100	98	90
Tear resistance	100	52	44
Abrasion resistance	100	162	96
Flex resistance	100	153	52
Rebound	100	108	115
Heat build-up	100	− 9° F.	− 14° F.

The consequence of this conclusion, substantiated by other workers, is that the United States Government arranged for new plants for the manufacture of such special furnace blacks for use with synthetic rubbers.

The implications of using the new furnace types of carbon black in the large quantities involved for GR-S is brought out by the statistics. According to the U.S. Bureau of Mines rubber manufacturers in 1943 used a total of 473 million lbs. of carbon blacks as against the previous peak of 439½ million lbs. in 1941. Furnace blacks comprised 36 per cent. of the total production as against 17 per cent. in 1941.

In 1946 the total black output was over 1,227 million lbs. Furnace black accounted for 625 million lbs. and for the first time exceeded channel black in quantity.

The excellent all-round character of these special furnace blacks

is brought out rather more clearly by Drogin's study of them in tread formulations based on Buna-S.

Most other fillers disperse without difficulty. It has been found that reinforcing pigments are absolutely essential to give satisfactory physical properties in the vulcanized material. It has been shown by McMahon and Kemp[15] that particle size is the predominating feature of the fillers used so far as reinforcement is concerned. Fine magnesia gave better tensile strength than coarse magnesium oxide; fine zinc oxide was better than coarse; finely powdered whiting was

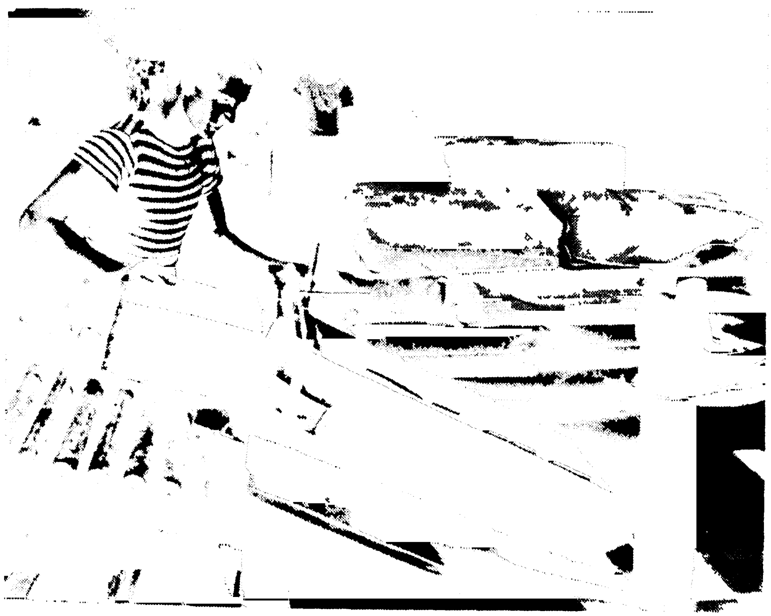


FIG. 72 – Packaging Bales of Finished Synthetic Rubber in Multiwall Bags for shipment to Consumers

superior to ordinary ground whiting. Apart from the black fillers several white fillers have proved interesting, notably hard clays, magnesium carbonate, surface treated whiting, and a few others. Until quite recently specially treated calcium carbonate of fine particle size was found to give good products. The calcium carbonate is surface-coated with stearic acid. Untreated calcium carbonate, such as whiting, gives very much inferior properties. Latterly, various types of hard clays have been found to give satisfactory results, more particularly as replacement for part of the blacks. It is claimed that a hard clay such as Suprex can replace up to 60 per cent. of furnace

black with improvement in the many properties such as tensile strength, elongation and tear resistance. Tensiles up to 2000 lbs. per sq. in. are obtainable. As in the case of natural rubber, hard clay is slower curing than softer clays, and rather greater quantities of curing agents are necessary. In GR-S optimum tensile strength is reached with an addition of 40 volumes of hard clay; whereas in natural rubber only a 10-volume addition is required. The tensile strengths obtained with hard clays approach those obtained with furnace blacks while the elongations remain relatively high.

TABLE 104. FILLERS IN GR-S

	Parts by weight
GR-S	100
RT 2332	20
Zinc oxide	5
Stearic acid	2
Pine tar	3
MBT	1
DPG	0·25
Sulphur	3
Filler	50

	H	M_{300}	TS	EB
Thermax	53	550	850	420
SRF	64	1200	1550	380
Whiting	50	330	420	350
Iron oxide	50	320	480	350
Clay (Stockalite)	56	570	1120	460
Winnofil	50	300	800	475
Silene	54	380	1200	580

It has been found that the addition of up to 10 parts of hard clay to a GR-S tread compound improves the resistance to cut. The cut-growth resistance approximates to that of a natural rubber tread, although it deteriorates somewhat after ageing. This is clearly a matter of great significance.

Silene is another American inorganic filler which has given very promising results. It is a white, finely divided calcium silicate. It gives tensile properties and other physical characteristics which are on a par with the semi-reinforcing blacks.

Effect of Fillers in GR-S. Using a tread type of mixing, the following behaviour was shown by a range of common fillers.

Kemp, Ingmanson, Howard and Wallder have examined the behaviour of fillers in GR-S insulating mixes, particularly from the

point of view of tensile properties. The formula used was as follows, with 27·7 volumes of filler added:

TABLE 105

Ingredient	Parts by weight
GR-S	100·00
Kadox 72	15·00
Mineral rubber	36·00
Stearic acid	0·75
Akroflex C	1·00
AgeRite White	1·00
Sulphur	4·00
Santocure	1·50
L 60	1·00

They found that hard clay and magnesia are the outstanding reinforcing materials of those evaluated. Unfortunately the use of these fillers is often limited to low-quality insulations because of their poor behaviour under moist conditions.

They showed that additions of organic extenders such as gilsonite or blown asphalt improved the tensile properties of GR-S appreciably. A GR-S compound containing no organic or mineral filler other than zinc oxide for activation was found to give poor tensile

TABLE 106. EFFECT OF FILLERS ON TENSILE PROPERTIES OF GR-S

Filler	Optimum cure at 134·5° C., Min.	Tensile strength, Lb./sq. in.	Elongation at break, %	Tensile at 300%, Lb. sq. in.
Dry ground whiting	20	820	570	195
Water-ground whiting	18	1100	680	130
TiO_2	12	1170	985	45
Iron oxide	12	1250	860	100
Coated pptd. whiting	15	1265	835	105
Al hydrate	15	1315	805	105
Zinc oxide	15	1375	815	105
Soft clay	25	1425	670	310
Zinc oxide	18	1440	745	140
Hard clay	25	1980	765	310
Extra light calcined magnesia	60	2440	670	500

strength of 520 lbs. per square inch in 5 minutes at 134·5° C. The tensile stress at 200 per cent. elongation was 50 lbs. With additions of 40 parts of gilsonite on the rubber content, the tensile strength increased to a maximum of 1115 lbs., and the tensile stress at 200 per cent. elongation increased to 210 lbs. With further additions of gilsonite

the tensile strength decreased slowly. The elongation at break decreased from 840 per cent. for the pure gum compound to 625 per cent. for the compound containing 40 parts of gilsonite. As the gilsonite content was increased, the time of cure required to attain maximum tensile strength increased from 5 minutes with the pure gum stock to 15 minutes for the compound containing 75 parts gilsonite.

Considering a different type of compound intended for light-coloured products, O'Brien[20] shows the following physical properties:

TABLE 107

	Parts by weight
GR-S	100
Filler	100
Sulphur	4
Softener	5
Coumarone resin	20
Mercaptobenzthiazole	2·5
D.O.T.G.	0·3
Zinc oxide	5
Colour	2·0

Filler	T_B	E_B
Coated fine-particle whiting	1700	600
Uncoated fine-particle whiting	1650	575
Zinc oxide	1640	610
Clay	1610	585
Iron oxide	1320	560
Super floss	890	450
Coated whiting	880	610

Carbon black—GR-S Latex. It has been made clear that with synthetic rubbers the incorporation of carbon black is even more essential than with natural rubber. Unlike natural rubber, synthetic rubbers of the GR-S type are not capable of giving high-quality pure gum stocks or high-grade light-coloured stocks. At present GR-S must be reinforced with carbon black or with a mixture of carbon black and other pigments if its physical properties are to be adequate for hard usage. Mixing carbon black into compound is a major part of the compounding operation.

One of the most interesting and most important developments in connection with GR-S has been the incorporation of compounding materials directly in GR-S latex. The idea has been to avoid the excessively long mixing times necessary for ordinary compounding. In the usual way, as compared with rubber, on a given machine one can mix a smaller batch of GR-S, taking a somewhat longer period. For a given output this clearly implies the need for much more plant and much more labour.

Apart from this it is a well-known fact that mill mixing achieves very indifferent dispersion of the filler. McMahon and Kemp have shown that direct admixture of fillers into latex effects much better dispersion.

Mixing carbon black directly into GR-S latex is already a major activity in the United States. O'Connor and Sweitzer [21] carried out much of the early work on the subject. They developed satisfactory technique for compounding GR-S in latex form, either with carbon alone or with carbon plus the other compounding ingredients. In their view latex compounding of GR-S results in notable improvements in stress-strain properties and improved reinforcement. This has not yet been fully justified in practice.

They found that latex compounding of GR-S resulted in outstanding improvements in heat-resistance properties, without any loss in rebound. The compounds produced gave lower modulus, higher elongation and higher subpermanent set.

In the ordinary way, adding carbon black to latex is beset with practical difficulties and the products do not show up the best properties. Much hinges on satisfactory dispersion. Rongone, Frost, and Swart [23] have described their successful work in this field. A good dispersion of carbon which blended readily with latex was obtained by the use of proper dispersing agents. The dispersion was readily made by mixing carbon black, water, and dispersing agent, and grinding them together in a ball mill or colloid mill.

The most specific dispersing agents for carbon black can apparently be divided into three classes : (1) condensation products of naphthalene sulphonic acid and formaldehyde, such as Darvan ; (2) the lignin sulphonic acids or salts, and (3) glucoside extracts such as quebracho extract, tannin extract, etc. All these are suitable for dispersing ordinary carbon blacks.

The carbon blacks to be dispersed presented individual problems because of particle size, state of aggregation, and the character of the surfaces, as well as the nature of the adsorbed gases. A rough test for the dispersing power of any agent was obtained by making a heavy paste of unpelletized carbon black and water on a glass plate and determining the total amount of dispersing agent and water required to transform a stiff paste to a fluid mixture.

It is important to use the minimum amount of dispersing agent to give a reasonably stable slurry that will blend readily with the latex.

The conclusion reached from this particular work was that if the size of the aggregates of carbon black were considerably less than some definite maximum (less than the bead size) when deposited with the

rubber, the shearing action of a pass or two through a mixing mill was sufficient to give good dispersion. Consequently, uncompressed black was stirred into water and dispersing agent with simple stirring, thus eliminating entirely the use of colloid mills and ball mills.

TABLE 108. PHYSICAL DATA ON CARBON BLACK COMPOUNDS

Compound No.	1	2	3	4	5	6
GR-S	100·00	100·00	100·00	100·00	100·00	100·00
EPC black (40 μ)	50·00	50·00	50·00	50·00	—	—
Fine channel black (30 μ)	—	—	—	—	50·00	50·00
Zinc oxide	5·00	5·00	5·00	5·00	5·00	5·00
Sulphur	2·00	2·00	2·00	2·00	2·00	2·00
Mercaptobenzothiazole	1·50	1·50	1·50	1·50	1·50	1·50
Softener (Bardol)	5·00	5·00	5·00	5·00	5·00	5·00
Softener (Turgum)	—	—	10·00	10·00	—	—
Filler dispersed	In latex	On mill	In latex	On mill	In latex	On mill

	Cure at 293° F. (min.)	Tensile strength (lbs. per sq. in.)	Stress at 300% elongation (lbs. per sq. in.)	Elongation at break (%)
Compound 1	40	3460	1270	580
	50	3640	1680	510
	60	3230	1890	440
Compound 2	40	3200	1060	625
	50	3245	1160	580
	60	3115	1215	530
Compound 3	50	3440	520	805
	60	3650	630	775
	75	3825	725	730
Compound 4	60	2545	400	850
	80	2750	505	795
	90	2960	585	745
	120	3235	775	725
Compound 5	80	3285	1100	625
	100	3615	1100	635
	120	3540	1195	620
Compound 6	40	3250	1050	610
	50	3315	1320	550
	60	3200	1300	525

The coagulation of a mixture of black and latex may be accomplished in numerous ways. Among them are the use of acid alone; a mixture of salt and acid; mixtures of salt, acid, and alum; alum alone and zinc chloride alone. Coagulation of the black latex is best accomplished by the use of a rapid, one-step coagulation rather than the

conventional method used for GR-S. This type of " shock " coagulation is best suited to entrap all the black in the coagulated rubber and to produce a clear mother liquid. A black crumb is formed which can be readily dried.

TABLE 109. PHYSICAL DATA ON ZINC OXIDE COMPOUNDS

Compound No.	1	2	3	4	5	6
GR-S						
Coarse zinc oxide (350 μ)						
Medium fine zinc oxide (190 μ)	—	—	100·00	100·00	—	—
Fine zinc oxide (120 μ)	—	—	—	—	100·00	100·00
Stearic acid	2·00	2·00	2·00	2·00	2·00	2·00
Sulphur	2·00	2·00	2·00	2·00	2·00	2·00
2-Mercaptothiazoline	1·00	1·00	1·00	1·00	1·00	1·00
Aldehydeamine	0·25	0·25	0·25	0·25	0·25	0·25
Filler dispersed	In latex	On mill	In latex	On mill	In latex	On mill

	Cure at 282° F. (min.)	Tensile strength (lbs. per sq. in.)	Stress at 300% elongation (lbs. per sq. in.)	Elongation at break (%)
Compound 1	15	1660	205	950
	20	1840	295	810
	25	1780	350	730
Compound 2	20	265	40	1475
	30	865	120	1030
	40	830	165	790
Compound 3	15	1900	190	895
	20	1790	240	765
	25	1960	300	740
Compound 4	15	1395	115	1015
	20	1480	125	855
	30	1280	185	695
Compound 5	10	2075	370	750
	12·5	2440	450	735
	15	2000	540	585
Compound 6	12·5	1395	220	780
	14	1440	260	735
	16	1325	265	665

This work showed that it was possible to make a cheap, satisfactory slurry of carbon black, which could readily be mixed with latex. The mixture could be coagulated to produce a black rubber which has properties at least as good as those of GR-S into which carbon black had been incorporated by the conventional mill method.

Table 110. Physical Data on Calcium Carbonate Compounds

Compound No.	1	2	3	4	5	6	7	8
GR-S	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Extra fine $CaCO_3$ (100 μ)	95·00	95·00	—	—	125·00	125·00	—	—
Fine $CaCO_3$	—	—	—	—	—	—	125·00	125·00
Medium fine $CaCO_3$ (600 μ)	—	—	91·00	91·00	—	—	—	—
Zinc oxide	5·00	5·00	5·00	5·00	5·00	5·00	5·00	5·00
Stearic acid	2·00	2·00	2·00	2·00	1·00	1·00	1·00	1·00
Sulphur	2·00	2·00	2·00	2·00	2·00	2·00	2·00	2·00
2-Mercaptobenzothiazole	1·00	1·00	1·00	1·00	—	—	—	—
Aldehydeamine	0·25	0·25	0·25	0·25	—	—	—	—
Paraffin	—	—	—	—	2·00	2·00	2·00	2·00
Akroflex-C	—	—	—	—	1·00	1·00	1·00	1·00
Agerite white	—	—	—	—	1·00	1·00	1·00	1·00
Heliozone	—	—	—	—	2·00	2·00	2·00	2·00
Softener (Turgum)	—	—	—	—	10·00	10·00	10·00	10·00
Ethyl selenac	—	—	—	—	1·00	1·00	1·00	1·00
Altax	—	—	—	—	1·50	1·50	1·50	1·50
Filler dispersed	In latex	On mill	In latex	On mill	In latex	On mill	In latex	On mill

	Cure at 282° F. (min.)	Tensile strength (lbs. per sq. in.)	Stress at 300% elongation (lbs. per sq. in.)	Elongation at break (%)
Compound 1	12·5	1800	260	855
	15	1995	325	830
	20	2110	415	755
Compound 2	15	1730	190	950
	20	1770	220	850
	30	1670	240	760
Compound 3	80	965	85	1060
	120	1120	125	895
	150	1175	105	915
Compound 4	15	690	85	870
	20	700	110	725
	30	620	170	630
Compound 5	16	1850	290	780
	17·5	1990	330	715
	20	1985	400	645
Compound 6	14·5	1270	145	930
	17·5	1500	280	635
	20	1400	355	540
Compound 7	10	1210	180	900
	11·5	1555	280	715
	13	1475	315	615
Compound 8	12	1010	170	875
	13	1100	235	725
	14	1035	285	615

Besides giving improved quality there are a number of practical advantages gained by the use of black GR-S:

1. The black-latex mixture can be handled in essentially the same way as normal GR-S throughout the various steps of coagulation, washing, drying, and baling.
2. By incorporating black into GR-S latex, an increase in milling capacity of about 35 per cent. is possible.
3. The total power required for mixing this black rubber is at least 20 per cent. less than for tread stock mixed in the conventional way.
4. Mixing temperatures are lower for latex-black stocks.
5. Physical properties and preliminary tyre tests show that carbon black incorporated with the latex produces stock equivalent in physical properties to stocks prepared by mixing carbon black into dry rubber.
6. Considerable savings are made possible by the use of this method.
7. The amount of dirt now present in the millrooms of the rubber manufacturing plants should be greatly reduced. This is a matter of considerable importance.
8. Black latex crum may provide a convenient form of compounded GR-S for processing.

McMahon and Kemp have published work on the tensile properties of compounds in which the fillers have been conventionally mill-mixed on the one hand, and directly mixed into the latex on the other hand. They confirmed that the direct latex-filler method gave far superior results all round.

Electrical Properties of GR-S. The most important application of GR-S, after tyres and inner tubes, is its use for cable insulation. A great deal of work has been done on its characteristics in this field. The importance of effective substitution for rubber is self-evident.

They were claimed to be superior to natural rubber. The great volume of work which has been carried out on GR-S, while it does not support the claims that GR-S is as good as rubber electrically, nevertheless confirms that it is a useful material. Moreover, GR-S is finding widespread application in the cable industry both for insulation and for sheathings.

The Vanderbilt Company[24] examined the properties of a number of insulation compounds applied on wire. The trend in this field is for the continuous vulcanization of coverings. The work was carried out by passing the Buna-S mixes through a 100-foot tube at 200 lbs. steam

pressure. The results illustrated in the tables confirm the suitability of Buna-S compounds for insulation coverings.

Latterly, Kemp, Ingmanson, Howard and Wallder have carried out intensive investigation as to the suitability of GR-S for insulation.

TABLE 111. INSULATION MIXES [20]

	B 4	A 7	B 7	X
Buna-S	100	100	100	—
Smoked sheet	—	—	—	100
Stearic acid	0·75	0·75	0·75	0·75
Agerite resin D	3	3	3	3
Zinc oxide	15	15	15	15
Mille mar	36	—	36	36
Whiting	90	—	—	90
Kalite No. 1	33	25	25	33
Kalvan	—	100	100	—
Tysonite	—	36	—	—
Litharge	1	5	5	9
Selenac	4	—	4	—
Altax	—	0·5	—	0·5
Methyl zimate	—	0·5	—	0·5
Sulphur	—	2	0·75	2
Vulcanization	300 ft./minute	300 ft./minute	450 ft./minute	450 ft./minute

TABLE 112. ELECTRICAL PROPERTIES OF BUNA-S—INSULATION MIXES [20]

Type	S.I.C.	Power factor	S.I.C.	Power factor	S.I.C.	Power factor	S.I.C.	Power factor
	Measured in mercury at 25° C.		After 24 hours' immersion in water at 50° C.		After 3 days' immersion in water at 50° C.		After 14 days' immersion in water at 50° C.	
B 4	2·84	0·0065	3·36	0·0301	3·51	0·0324	3·76	0·0396
A 7	3·69	0·0118	4·03	0·0251	4·16	0·0286	4·43	0·0305
B 7	3·16	0·0114	3·39	0·0114	3·51	0·0132	3·71	0·0148
X	2·81	0·0058	3·22	0·0208	3·31	0·0226	3·48	0·0235

They first showed that different grades of GR-S varied according to the source of manufacture. They illustrated that water-extractable materials had considerable influence on the electrical characteristics. They concluded that there was a general relation between moisture absorption of the raw polymer and the electrical stability of the vulcanized GR-S insulation.

They compared the electrical characteristics of unvulcanized GR-S samples with unvulcanized natural rubber. They found that the dielectric constant and power factor of unvulcanized GR-S were about the same as for natural rubber. The values for specific resistivity were somewhat lower. When vulcanized the value of these characteristics were found to be of the same order as for similar vulcanized rubber stocks.

TABLE 113. ELECTRICAL CHARACTERISTICS OF BUNA-S COMPARED WITH SMOKED SHEETS, DRY AND WET

	Days in water	% Weight gain	Dielectric constant	% Power factor	Specific resistivity, Ohm-cm.
GR-S, A	0	0	2·39	0·11	$1·1 \times 10^{14}$
	7	1·91	2·59	0·35	$8·2 \times 10^{12}$
GR-S, B	0	0	2·49	0·23	$1·5 \times 10^{15}$
	7	6·46	2·92	0·33	$2·1 \times 10^{13}$
GR-S, C	0	0	2·50	0·14	$6·8 \times 10^{14}$
	7	2·62	2·68	0·27	$1·7 \times 10^{14}$
Smoked sheets	0	0	2·45	0·35	5×10^{15}
(milled)	7	2·10	2·84	4·19	5×10^{15}

Reclaimed GR-S. Vulcanized GR-S is being reclaimed on an ever-increasing scale. The actual volume of reclaimed material is not yet very great in relation to the output of ordinary reclaimed rubber. However, it is likely to increase substantially as the quantities of vulcanized GR-S grow. The vulcanized synthetic rubber cannot be plasticized by the usual thermal or alkali process used with rubber. Straightforward application of heat causes GR-S to become brittle, while alkali conditions have an equally objectionable result. The predominating methods are therefore combinations of the use of chemical plasticizing agents together with intensive mechanical treatment. It has been necessary to find chemicals which would act as active reclaiming agents. Materials which are used include aryl mercaptans and high molecular weight aliphatic amines. Alkylated phenol sulphides [14] are also effective. The use of such agents, together with correct swelling agents and tackifiers, has resulted in excellent reclaims.

For the production of whole-tyre GR-S reclaim it is necessary to remove the tyre cords with dilute zinc chloride solution. A consequence of the absence of alkali is that GR-S whole-tyre reclaim is much slower curing than its natural counterpart.

One such method of preparing a plastic sheet from vulcanized GR-S has beeen described by Twiss, Amphlett and Hughes.[27] They grind the GR-S to fine particles, and then subject these to intensive mechanical working on the mixing-mill between 60° C. and 120° C. They add up to 10 per cent. of a softener such as pine oil, pine tar, or coumarone resin. According to them a tread-type GR-S when reclaimed in this manner, and then used to make up a tyre tread, was found to possess wearing properties only inferior to those of the original material. They stated that the comparative wearing qualities of the two treads were approximately in the ratio of 75 : 100.

The Wingfoot Corporation[32] have described a method for reclaiming butadiene rubbers.

TABLE 114. COMPARISON OF ELECTRICAL CHARACTERISTICS OF VULCANIZED GR-S GUM STOCKS AND A NATURAL RUBBER GUM COMPOUND

Elastomer	Days in water	% Weight gain	Dielectric constant	% Power factor	Specific resistivity, Ohm-cm.
GR-S, A . .	0	0	2·72	0·16	$3 \cdot 84 \times 10^{14}$
	7	0·92	2·78	0·41	$1 \cdot 22 \times 10^{14}$
GR-S, B . .	0	0	2·72	0·17	$8 \cdot 05 \times 10^{14}$
	7	1·94	2·95	0·89	$2 \cdot 00 \times 10^{14}$
Pale crepe . .	0	0	2·68	0·22	1×10^{16}
	7	1·42	2·94	0·26	1×10^{16}

GR-S	100
Zinc oxide	—6
Stearic acid	1
Sulphur	2
L 60 (a benzothiazyl material)	0·5
Benzothiazyl 2-monocyclohexyl sulphonamide (Santocure)	0·5

Vulcanized 60 minutes at 134·5° C.

Vulcanized material is ground fine as usual and treated with a coal-tar oil. It is then plasticized with a carboxylic acid, e.g. acetic acid, butyric, tannic, etc. Or an alcohol such as methyl, ethyl, etc., may be used. The material is thereafter ready for use as reclaim.

GR-S reclaim has physical properties which are not greatly different from that of natural rubber reclaim. It is less tacky and rather deader, but can be loaded in much the same way, and gives smoother and more

Table 115. Mechanical Mixes based on GR-S

Hardness (Shore)	65	80	65	50	65	55
GR-S	100	100	100	100	100	100
Reclaim	—	—	140	—	—	—
Channel Black EPC	50	—	75	—	—	—
Thermal Black MT	—	150	—	—	—	—
Furnace Black SRF	—	—	—	30	—	60
Zinc Oxide	5	5	10	5	100	5
Clay	—	—	—	—	100	—
Magnesia	—	—	—	—	5	—
Softener	3	3	5	3	—	3
Mineral oil	—	5	—	—	—	5
Extender	—	—	10	—	—	—
Coumarone Resin	—	—	—	—	5	—
Stearic acid	1	1	1·5	1	—	1
Antioxidant	—	1	2	2	—	1
Sulphur	2	2·25	4	2·25	2	2
Thiuram Monosulphide	0·5	0·75	0·5	0·65	0·2	0·6
Temp. C.	135	141	135	141	141	141
Cure—Minutes	55	30	30	30	60	30
T_B	3,100	2,020	2,000	750	1,000	1,700
E_B	650	150	600	460	750	525
M_{300}	950	—	810	430	350	900

Table 116. GR-S Tyre Reclaim in New Compounds

GR-S	100	70	70
Tyre reclaim	—	55·5	—
GR-S Tyre reclaim	—	—	60
E.P.C. black	43	35	35
Stearic acid	2	2	2
Coal tar	4	4	4
Pine tar	2	2	2
Zinc oxide	3	3	3
S.	1·75	2	2
Santocure	1	1	1

	M_{300}	T_B	E_B	M_{300}	T_B	E_B	M_{300}	T_B	E_B
30 mins. at 292 F.	500	2100	780	800	1550	500	600	1550	650
45 ,, ,, ,,	600	2350	720	828	1600	520	700	1750	615
60 ,, ,, ,,	700	2400	690	825	1550	500	700	1850	605
75 ,, ,, ,,	650	2350	670	800	1500	510	725	1800	565
Oven Ageing 70 Hours at 100° C.									
30 mins. at 292° F.	1350	1900	350	—	1475	280	1475	1800	360
45 ,, ,, ,,	1400	1900	360	1350	1800	310	1400	1800	370
60 ,, ,, ,,	1400	1900	375	1275	1500	330	1425	1825	385
75 ,, ,, ,,	1425	2000	400	1250	1550	345	1400	1875	400
Abrasion (du Pont Abrader)									
45 mins. at 292° F.	92%			72%			84%		

c.c. loss per H.P./hour.

easily extruded materials. Satisfactory soft and hard compositions can be made up with such reclaims used in the place of ordinary rubber reclaim.

Busenberg[3] has made an interesting and valuable study of synthetic rubber reclaims. He has illustrated the value of GR-S reclaims in new GR-S compositions. He compared the analysis of a GR-S whole-tyre reclaim with an ordinary whole-tyre reclaim.

Ecker and Gumlich[7] have described a method for reclaiming GR-S by heating in the presence of an aromatic mercaptan at a temperature of 130°–150° C. in an atmosphere containing oxygen at a higher pressure and concentration per cubic centimetre than is normally found in the atmosphere.

Busenberg summarized the outstanding features of GR-S reclaim as follows:

Advantages of GR-S Tyre Reclaim.

(1) Comparable with natural reclaim.
(2) Melting, calendering and extruding characteristics very good. Smoothness, compactness, ability to hold shape.
(3) Lack of tack sometimes an advantage.
(4) Carbon content is high.
(5) May be used as part replacement, of rubber, GR-S, or reclaim in GR-S stocks.

Disadvantages.

(1) Slower rate of cure.
(2) Lack of tack sometimes a disadvantage.

Cyclized GR-S. The preparation of chemical derivatives of GR-S is a matter of some potential interest. Whereas natural rubber may be cyclized by treating a boiling benzene solution with a catalyst, such as chlorostannic acid, GR-S requires the much higher temperatures obtainable in such solvents as phenol, cresol, neutral coal-tar oils, and naphthalene. According to Endres the procedure consists of heating a 10 to 15 per cent. solution of GR-S in one of the above solvents to a temperature of 160° to 180° C., and adding the proper amount of catalyst with agitation. After approximately 10 minutes the temperature begins to rise, and the viscosity of the solution increases to form a gel. The temperature then decreases and the viscosity is reduced until, after about 30 minutes, the reaction mixture becomes a thin brown-coloured solution, from which the cyclized GR-S may be recovered by steam distillation or extraction of the solvent.

Cyclized GR-S is a brown resin which is soluble in aromatic and chlorinated hydrocarbons, but insoluble in common organic solvents.

The procedure is quite flexible, and changes in one condition can be compensated by changes in another.

For example, an increase in the amount of catalyst employed increases the rate of reaction and accomplishes the same result at a lower temperature. The hardness and softening point of the product depends on the time of reaction in much the same manner as in the case of natural rubber and can be varied from soft and rubbery with softening point of 55° C., to a hard and brittle resin, having a softening point of 105° C. Correspondingly, the iodine number dropped from 350 for GR-S to 180 in the hard cyclo-GR-S. Analogous to the natural rubber reaction, a product of desired softening point may be obtained by stopping the reaction at the proper viscosity.

Various cyclizing agents or catalysts have been studied, and chlorostannic acid, stannic chloride and boron trifluoride have been found to be effective in the solvents mentioned. By heating GR-S in 10 per cent. solution in naphthalene with 15 per cent. of its weight of concentrated sulphuric acid for 3·5 hours at 180° C., a hard rubbery product was obtained. Hydrogen chloride does not produce a resinous product at 180° C. as it does with natural rubber.

The low moisture-vapour transmission of this material suggests its use in moistureproof coatings for paper. Such coatings are clear and transparent, and impart no taste or odour. The material shows promise also as an ingredient in moisture-, alkali-, and acid-resisting paints and lacquers, and as a reinforcing agent in GR-S wire-coating compounds.

Manufacture of Articles from GR-S. The stage has now been reached where virtually the whole range of articles made in rubber are being made on the basis of GR-S. The position is rapidly being attained where GR-S alone is being employed ; that is to say, without any addition of natural rubber or of natural reclaim. Obviously by far the greatest amount is being used in the production of tyres. This particular problem has been given the maximum possible amount of attention. However, a wide variety of other products—cable coverings, mechanical goods, surgical goods, sponge rubber, hard rubber, etc.—are now being made on the basis of GR-S. The knowledge gained in the production of tyres has been applied to these other forms of manufacture.

While most types of tyres have in general proved to be slightly inferior to natural rubber tyres, in some instances they are now better than similar tyres made before the war.

Many mechanical goods made from GR-S are considered to be superior to the comparable natural rubber articles.

It is interesting to consider a typical procedure for the manufacture of tyres since this points the way for the production of other rubber articles. Hardman [9] has given a very interesting account of the methods adopted in using GR-S to make tyres. Most of the problems encountered with GR-S are involved.

According to Hardman the most satisfactory procedure appears to be to make up the rubber with black in master batch form, which can be done very satisfactorily in a No. 11 Banbury in about 300- or 400-lb. batches, and if part of the stearic acid is included in the master batch the dispersion is improved. This should be added a little at a time along with the black, which should be added in three or four lots in order to avoid any tendency to cyclization, which is liable to occur if the black is added too quickly, giving the appearance of scorched rubber when on the mill. About 30 minutes in a Banbury is sufficient, followed by 20 minutes mixing on a well-cooled 84-inch mill to improve the dispersion and effect further breakdown. The master batch may then be batched out and dipped. Of course at the present time there is a strong trend towards the use of master batches of latex GR-S and carbon black. After standing for about 12 hours it is ready for making up into the finished compound. In some cases there is a further period of standing prior to final mixing. For the actual mixing, reclaim, if any, should be masticated separately, and then dropped on the tray while the master batch, which should be given a severe handling on a tight mill, is broken down ; the reclaim will then disperse satisfactorily. The softeners and inorganic ingredients should be added next, together with the accelerator and antioxidant, and when these are thoroughly well dispersed the sulphur may be incorporated, for which operation the retention of a little of the oil may be considered advisable. About 30 minutes is the usual mixing time.

In large-scale practice it has been found that mixing in the internal mixer such as a Banbury is cheaper with GR-S than with rubber. This is because it requires no breakdown as in the case of raw rubber. Fillers can be added directly with the GR-S.

Scorching is no problem with synthetics. According to Hardman, compounded GR-S stocks keep fairly well. Tread stock should be used within three days of mixing. If kept longer than this they tend to become difficult to handle, developing too much heat in the extruder and giving uneven sections. Older stocks should be remilled on a tight cold mill and allowed to cool thoroughly before being used, otherwise the effect of remilling will be partly nullified. Chalking is of course necessary to prevent sticking in the storage racks.

The compounds must be well broken down, but they calender very

satisfactorily, where the thickness of the sheet does not exceed $\frac{1}{64}$ inch. Above this thickness the sheet gets progressively rougher. This roughness does not seem to have any detrimental effect in building, and disappears in cure. It is good practice to make thicker sheets by plying. Calendered sheet shows little calender grain, the stretch being about the same in either direction.

For sheeting and the coating of fabrics the top bowl should be about 210° F., and the middle about 190° F. The sheet, although not so tacky as with good quality natural rubber stocks, shows little deterioration in this respect, even when stored for several months, nor does it show any appreciable sign of bloom. For frictioning, somewhat higher temperatures are required, i.e. top 230° F., middle 235° F., and bottom 225° F. The standard calender friction ration of about 3 to 2 is satisfactory. Pretreatment of the cotton appears to improve adhesion. The cotton must be well dried and the bottom bowl temperature is maintained to ensure good penetration.

Extruding Treads. As usual, for extrusion the compound must be well broken down. Extruding appears to be the only satisfactory method of preparing treads, as profiling tends to cause disintegration. For the best results the compound should be used about 24 hours after mixing, being well broken down on a cool mill after at least three passes through a breaker. During the inevitable intervals which occur while dies are being changed or adjusted it should be cut out and allowed to cool rather than run round the mill. Other things being equal, the section appears to become heavier as the temperature rises. The barrel and worm of the extruder should be well cooled, but the head and die should be about 215° F. Dies having a long taper seem to be the most suitable and give the most satisfactory results. At the extruding temperature the edges of the tread sections tend to break owing to the softness of the stock. As with mixing, the output of an extruder is considerably reduced, although this difference is now being levelled out. To keep production at normal levels additional extrusion capacity is required.

As a general rule, extrusion presents some problems. The disadvantages are : high shrinkage, poor surface appearance, rough tubing and excessive swellings. Existing dies for rubber are unsuitable because GR-S compounds swell rather more. The die aperture for GR-S is therefore usually about three-quarters the size used with rubber.

Juve[11] has made an interesting study of the extrusion behaviour of comparable synthetic rubber compositions. His figures illustrate the slower extrusion attained with GR-S.

In actual tyre building, the outstanding problem is the serious lack

TABLE 117. COMPARATIVE EXTRUSION CHARACTERISTICS

	Compounded stock—4 min. Mooney. S R.	Volume extruded per minute cu. cm.	Factory extrusion. No. 2 Royle tubing machine. Length extruded per minute, feet	Relative swell
Natural rubber	29	762	20·7	1·0
GR-S	37	305	8·5	0·97
GR-M	32	622	19·2	0·88
GR-I	36	376	9·3	1·1

of tackiness during actual building, and the extra time and care required. Fairly good results can be obtained with compounds containing a proportion of natural rubber and reclaim, and something approaching normal procedure can be maintained, but even so, whilst the plies adhere fairly well, the surfaces do not seem to coalesce anything like so completely as with natural rubber. Extruded treads with more than 75 per cent. GR-S require a varnish coat of ordinary rubber solution to aid adhesion.

Petrol seems to be as good as anything for swabbing, but it must be supplemented by liberal use of the wire brush, as no solvent appears to do anything more than bring the oils and resins incorporated in the mix to the surface. The usual solvents seem to be quite incapable of dissolving the actual polymer, and this probably accounts for the necessity for so much rolling down, as the adhesion provided by the softeners present is insufficiently strong to hold the plies together if there is any natural tendency for them to lift owing to the contour of the drum on which the tyre is being built.

According to Hardman, application of treads during tyre building has its own special problems. These cannot contain the same high proportion of softener as the carcass stocks. In order to get adhesion,

TABLE 118. PHYSICAL PROPERTIES OF PRESS-CURED AND EXTRUDED PRODUCTS

	Press-cured products				Extruded products			
	M_{200}	T_B	E_B	H	M_{200}	T_B	E_B	H
Natural rubber	420	2850	555	53	720	2750	480	53
GR-S	450	900	300	58	400	790	300	53
GR-M	600	2315	545	65	800	2330	455	58
GR-I	320	1450	665	65	330	1120	757	52

it is essential to wire buff them thoroughly after swabbing them with petrol.

To make a satisfactory splice it is often necessary to insulate the faces of the skive with a thin sheet of natural rubber compound which should be turned under for about one inch. Even with all these precautions the tread is always liable to spring away under the action of the centrifugal force if the drum is run fast before the stitchers have been applied. Quite good results can be obtained if the underside of the tread and the last ply of the carcass are coated with natural rubber cement. Alternatively, the last ply may be insulated with a thin sheet of natural rubber compound and similarly with the underside of the tread. Better practice is to calender the latter on hot at the time of extruding, there being then very little trouble with adhesion.

Synthetic treads may be applied quite satisfactorily to natural rubber carcasses, the adhesion in the finished product being of the same order as that obtained with an ordinary tread.

GR-S tyres cure very satisfactorily, and indeed this is about the only stage at which normal procedure can be fully maintained. The extraction of the moulded tyres sometimes offers difficulties.

The methods employed in making up tyres apply equally well to other products. After all, compounds approximating to tread rubber are used for making conveyor belts, cable sheathing, hose covers, etc. They all involve similar problems of mixing, sheeting, plying, extrusion, etc.

In the production of moulded articles until comparatively recently only black compounds were made. This was due to the fact that strong rubbers were only obtained when a substantial loading of carbon black was present. Without black the tensile properties were extremely poor. Latterly several white pigments have appeared which in GR-S give reasonably strong products, so that coloured articles now become possible. The whole range of mechanical goods is now being manufactured on the basis of GR-S.

Moulded GR-S articles tear much more readily than corresponding rubber articles, especially when hot. It is desirable to have little nerve and considerable hot strength. GR-S is bad in both these respects compared with rubber.

This implies that the extraction of articles from mould may often give difficulty.

Sponge Rubber. GR-S is being used to make various general-purpose sponge-rubber items which were formerly made from natural rubber. There is no difficulty in making the numerous items in ordinary everyday use. The compounding and processing features are much the same as with natural rubber. That is to say, large amounts

ofteners must be incorporated, while gas-evolving agents such as ionium carbonate, sodium carbonate, diazoaminobenzene, etc., are added. It can be compounded to be more easily compressible at subzero temperatures than any other synthetic rubber, and closely resembles natural rubber in this respect. It can likewise be compounded to have good resistance to heat ageing. One company reported that the difficulty of calendering thick sheets of GR-S stock had limited their production for the time being to 0·25-inch thick finished sponge rubber sheets. Hard synthetic (ebonite) sponge rubber is being made from GR-S. These hard sponge rubber products are very similar to those made from natural rubber and in some properties, notably tensile and impact strength, are even superior. They find many uses as floats, insulation materials, etc.

REFERENCES

1 BARKER, *Rubber, History, Production and Manufacture*, U.S. Dept. of Commerce, 1940.
2 BRUCE, LYLE and BLAKE, *Rubber Chem. Tech.*, 1944, **17**, 410.
3 BUSENBERG, *Rubber Age* (N.Y.), 1945, **56**, 181.
4 CHEYNEY and ROBINSON, *Ind. Eng. Chem.*, 1943, **35**, 976.
5 COTTON, *India Rubber Journal*, 1947, **113**, 179
6 DROGIN, *Rubber Age* (N.Y.), 1942, **5**, 483.
7 ECKER and GUMLICH, U.S.P. 2,338,427/1943.
8 GARVEY, WHITLOCK and FREESE, *Ind. Eng. Chem.*, 1942, **34**, 1309.
9 HARDMAN, *India Rubber Journal*, 1944, **107**, 3.
10 HENDRICKS, *Rubber Age* (N.Y.), 1944, **54**, 521.
11 JUVE, *Rubber Chem. Tech.*, 1944, **17**, 932.
12 JUVE and GARVEY, *Ind. Eng. Chem.*, 1944, **36**, 212.
13 KEMP, INGMANSON, HOWARD and WALLDER, *Ind. Eng. Chem.*, 1944, **36**, 368.
14 KILBOURNE, COOK, ALBERT and SMITH, *Ind. Eng. Chem.*, 1948, **40**, 1194.
15 MCMAHON and KEMP, *Rubber Chem. Tech.*, 1945, **18**, 22.
16 MASSIE and WARNER, *Rubber Age* (N.Y.), 1944, **55**, 56.
17 Ministry of Supply, Manufacturers' Memorandum M.14, p. 5.
18 MORRIS, MITTON, SEEGMAN and WERKENTHIN, *Rubber Chem. Tech.*, 1944, **17**, 704.
19 NEAL and OTTENHOFF, *Ind. Eng. Chem.*, 1944, **36**, 352.
20 O'BRIEN, *India Rubber World*, 1945, **112**, 561.
21 O'CONNOR and SWEITZER, *Rubber Age* (N.Y.), 1944, **54**, 423.
22 PRETTYMAN, *Ind. Eng. Chem.*, 1944, **36**, 29.
23 RONGONE, FROST and SWART, *Rubber Age* (N.Y.), 1944, **55**, 577.
24 R. T. Vanderbilt Co., *India Rubber World*, 1942, **106**, 453, 572 ; 1942 ,**107**, 36.
25 SHELTON and WINN, *Rubber Age* (N.Y.), 1944, **55**, 63.
26 STURGIS, BAUM and VINCENT, *Ind. Eng. Chem.*, 1944, **36**, 348.
27 TWISS, AMPHLETT and HUGHES, B.P. 564, 514/1944.
28 VILA, *Ind. Eng. Chem.*, 1942, **34**, 1269.
29 VILA and HOLBROOK, *India Rubber World*, 1943, **109**, 37.
30 WIEGAND and BRAENDLE, *Ind. Eng. Chem.*, 1944, **36**, 702 ; 1944, **36**, 727.
31 WILLSHAW, *India Rubber Journal*, 1945, **108**, 15.
32 Wingfoot Corporation, B.P. 558,334/1944.

CHAPTER 14

MODIFIED GR-S POLYMERS AND LATICES

THE production of synthetic rubber on the massive scale so successfully attained in the United States introduced innumerable problems. With the passing of time many of these have been resolved. Side by side with production, intensive research and development work has been carried out. All the results were pooled and there was a complete exchange of information. The problem of scale of production having been solved there was the urgent question of uniformity. By dint of rigid specifications the products of the numerous plants eventually attained a reasonable degree of uniformity. Early experiences were frequently exasperating when successive deliveries of material showed entirely different behaviour. According to Hicks,[2] in a period of five years there were no fewer than 4,000 reports from producers, consumers, research workers, etc.

As a result there gradually emerged a distinct pattern. Standard GR-S was suitable for many applications. Its shortcomings were fully appreciated. For some applications new materials were essential. The research workers provided a steady stream of new materials. These each had to be subjected to the routine cycle of tests—through pilot plant, manufacturing unit, and product test. From the vast number of materials produced, a fairly considerate number showed promise and were given extended trials. Most of course were eliminated as useless—there is always a high wastage in scientific and development work. The remorseless process of elimination still continues. As the endless stream of new products were gradually sifted out, relatively few emerged which showed high promise. Specialized materials which admirably answered specific requirements came through all their trials and were put into large-scale production. So that to-day the production of variations of GR-S is nearly as large as the production of standard GR-S. And the research work still goes forward without any loss of impetus.

Available GR-S Polymers. Standard GR-S is the all-purpose polymer which has been produced to the extent of 2,241 long tons in 1942, 181,470 long tons in 1943, 668,840 long tons in 1944, and 754,345 long tons in 1945. It is remarkable that despite lack of any large-scale experience no appreciable change in the polymerization formula or reaction conditions has been required since production

began in May 1942. In addition, the progressive replacement of natural rubber with GR-S during that period did not require sacrifice of important characteristics in the majority of the rubber products.

In the United States production of GR-S the first problem was to get an adequate production of the standard material, whatever its faults. When this task had been completed, attention was given to the need of special polymers for applications where rubber could not be satisfactorily replaced. Brady [1] has admirably summarized these in seven groups—

1. Polymers of different viscosities.
2. Polymers with enhanced tackiness.
3. Non-discolouring, non-staining types of GR-S.
4. Low water-absorption polymers.
5. Super-processing polymer.
6. Masterbatches of black fillers.
7. Latices.

POLYMERS OF DIFFERENT VISCOSITIES

	Polymer composition	Mooney viscosity	Contained stabilizer
GR-S-45AC	76·5% butadiene 23·5% styrene	45	Non-discolouring Non-staining
Standard GR-S	76·5% butadiene 23·5% styrene	50	Discolouring Staining
GR-S-AC	76·5% butadiene 23·5% styrene	50	Discolouring Staining
GR-S-85	76·5% butadiene 23·5% styrene	100	Discolouring Staining

(Mooney large rotor, 4-minute reading, 212° F.)

Standard GR-S. While Standard GR-S continues to be the most widely used GR-S polymer, it is slowly losing that position to some of the newer types. The total production of the variations almost equals the Standard GR-S production.

GR-S-AC. The standard coagulant used in GR-S production is first a concentrated solution of sodium chloride and then a dilute solution of sulphuric acid added to the latex. The salt starts coagulation and controls the particle size of the floc, the acid completes the coagulation and converts the soap in the polymer to fatty acid.

A second method of coagulation employs a solution of alum to precipitate the polymer from the latex. Where alum is used the polymer has AC added to its name.

Alum coagulation is sometimes used to impart desired characteristics such as viscosity, stability, or low ash content or water resistance. Generally it is used when the salt-acid method has caused difficulties

in the finishing of polymers during the coagulating and dewatering operations.

GR-S-45-AC. This is one of the latter type. It is a 45 Mooney variation made principally for use in chemically blown sponge compounds. In this application it has largely superseded Standard GR-S because it requires less mill mastication and less plasticizer and permits the production of low-density sponge. It has the additional advantages of being pale in colour, free from tendency to discolour during exposure to light, and free from any tendency to stain other materials.

GR-S-85. GR-S-85 is a 100 Mooney variation with limited uses. It was developed to meet the requirements of the asbestos-sheet-packing industry when it was found that standard GR-S was not a satisfactory replacement for the natural rubber and could not be used without sacrificing important processing and performance characteristics. GR-S-85 permitted the complete replacement of natural with synthetic without loss of processability and manufacturing efficiency. It has, moreover, permitted the production of sheet packings which are better than those made with natural rubber. It has also been used for car brake linings. It is somewhat difficult to process.

POLYMERS WITH ENHANCED TACKINESS

	Polymer composition	Mooney viscosity	Contained stabilizer
GR-S-10	76·5% butadiene 23·5% styrene	55	Discolouring Staining
GR-S-10-AC	76·5% butadiene 23·5% styrene	55	Discolouring Staining
GR-S-16	76·5% butadiene 23·5% styrene	100	Slightly discolouring Slightly staining
GR-S-17	76·5% butadiene	55	Non-discolouring Non-staining
X-274	76·5% butadiene 23·5% styrene	60	Slightly discolouring Slightly staining
X-304	58% butadiene 42% styrene	85	Slightly discolouring Slightly staining

(Mooney large rotor, 4-minute reading, 212° F.)

GR-S-10. In composition GR-S-10 differs from Standard GR-S only in containing an equivalent quantity of fatty acid, both converted from the soaps used to emulsify the hydrocarbons for the polymerization reaction. In properties there is a greater difference; GR-S-10 is the better of the two in many compounds. The following advantages were found to be gained through its use in tyre manufacture:

1. Banbury output is increased by 20 per cent. through the use of concentrated masterbatches. This method of compounding was not possible with Standard GR-S because the master-

batches were dry and crumbly and not so easy to handle on the mill.

2. Better adhesion of the calender coat to the solutioned fabric before vulcanization has given many savings. Coating can be done at higher speed and there is an increase of 10–15 per cent. in calender efficiency. GR-S-10 compounds are also better for friction coating ; they adhere more strongly to the calender roll and do not sheer off on the fabric.
3. Greater tackiness for laminating and splicing, particularly in compounds containing natural rubber.
4. Better ply-separation resistance.
5. Higher heat-break resistance. Carcass compound with GR-S-10 runs cooler and is more resistant to shock.
6. Better abrasion and crack-growth resistance in tread compound. Road tests have indicated 5–10 per cent. improvement in wear with fewer groove cracks.

The value of GR-S-10 is not limited to tyres. It offers advantage in the compounding of many products such as soles and heels, conveyor and power transmission belts, bicycle tyres, hose, etc.

GR-S-10-AC. This material differs from GR-S-10 only in that it is a few points higher in Mooney viscosity and is coagulated from the latex with alum solution rather than with the standard salt and acid solutions.

GR-S-17. This polymer is a non-discolouring, non-staining variation of GR-S-10 especially made for use in white and light-coloured compounds which are required to retain their brilliance, and for all compounds which must not stain surfaces with which they may come into contact. Its similarity to GR-S-10 in properties and freedom from discolouring and staining tendencies make it valuable in the compounding of white sidewall tyres, white and light-coloured shoe soles and heels, electric lamp cord, many mechanical goods, hospital sheeting, etc.

X-274-GR-S. This type is intermediate between GR-S-17 and GR-S-10 in discolouring and staining tendencies.

GR-S-16. This high-viscosity polymer has been developed for use in the compounding of adhesives and pressure-sensitive tapes. Some of the advantages to be gained from the use of GR-S-16 in this application include :

1. Much higher raw material strength. High raw strength or cohesiveness is necessary to prevent transfer of the adhesive film from one surface to another and to give bonds which will not break when subjected to continuous low stresses,

2. Contains no fatty acid to bloom to the surface of the adhesive film and reduce its surface tackiness.
3. Non-discolouring. The stabilizer in GR-S-16 is low in discolouring tendency and does not darken appreciably during prolonged exposure to light. This is of importance in transparent-black tapes, stationery adhesives, and the like.

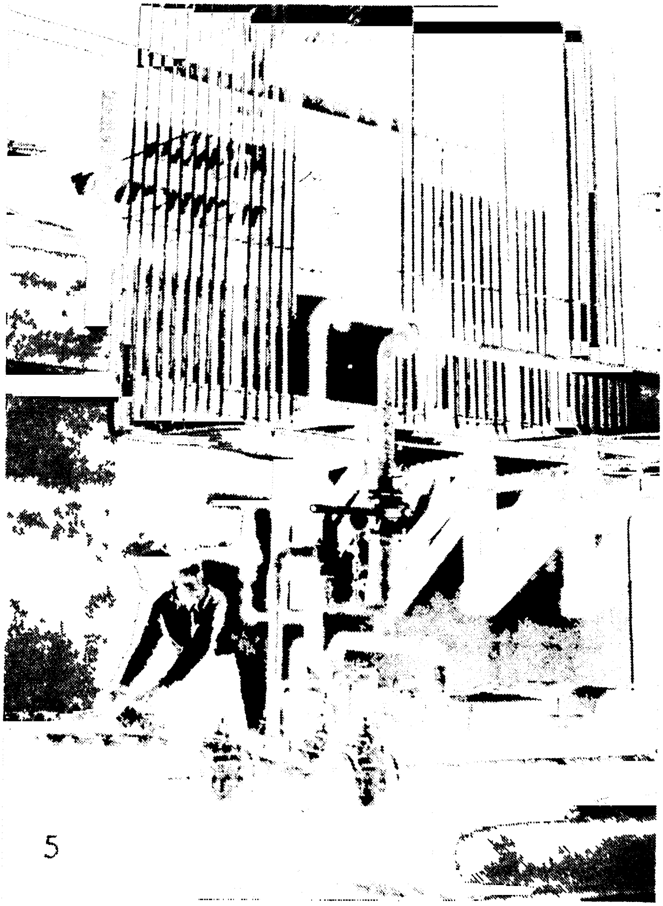


FIG. 73.—Blending Tanks

Many batches of synthetic rubber latex are batched and blended in 30,000-gallon concrete storage tanks at the Institute Plant. This blending assures uniformity of the product.

4. Low in electrolyte content. This is an important consideration in tapes made for electrical applications in which the adhesive will be in contact with corrosible metal surfaces.

GR-S-16 is made principally for use in unvulcanized form, but may also be used in compounds which are vulcanized. Because of the high initial viscosity of GR-S-16, compounds are difficult to process.

X-304-GR-S. Like GR-S-16, this is made principally for use in the compounding of adhesives and pressure-sensitive tapes.

NON-DISCOLOURING, NON-STAINING TYPES OF GR-S

	Polymer composition	Mooney viscosity	Contained acid	Rate of cure
GR-S-25	76·5% butadiene, 23·5% styrene	50	Fatty acid	Slower than Standard GR-S
GR-S-17	76·5% butadiene, 23·5% styrene	55	Rosin acid	Slower than Standard GR-S-10
X-274	76·5% butadiene, 23·5% styrene	60	Rosin acid	Slower than Standard GR-S-10
GR-S-45-AC	76·5% butadiene, 23·5% styrene	45	Fatty acid	Slower than Standard GR-S
GR-S-40-AC	58% butadiene, 42% styrene	45	Fatty acid	Slower than Standard GR-S
X-344	76·25% butadiene, 23·25% styrene, 0·5% crosslink	55	Fatty acid	Requires sulphur adjustment

(Mooney large rotor, 4-minute reading, 212 F.)

GR-S-25. This is a non-discolouring, non-staining variation of Standard GR-S especially made for use in white and light-coloured compounds which are required to be free from tendency to stain other materials. Its very pale colour and complete freedom from materials which can cause stain or discoloration make it ideal for numerous products such as white-sidewall tyres, white and light-coloured shoe soles and heels, mottled floor tile, cable on electrical household appliances, upholstery, tubing, door bumpers and gaskets, and hospital sheeting, and so on.

GR-S-17. Brady considered that GR-S-17 is preferable to GR-S-25 in most compounds, particularly those reinforced with minimum quantities of fillers, or made for use in dynamic service.

GR-S-45-AC. This is a polymer made principally for use in chemically blown sponge compounds to :

1. Reduce mill mastication requirements, increase mill capacity, reduce labour and power costs.
2. Facilitate blow to lower densities.
3. Obtain good colours with minimum concentrations of pigment. X-317-AC is pale in colour and required only small amounts of pigment.
4. Obtain colour stability.
5. Improve resilience of the sponge.
6. Obtain freedom from staining.

GR-S-40-AC. This is a high styrene polymer; the ratio of styrene combined with butadiene is nearly twice that of the other GR-S polymers. This difference in composition gives GR-S-40-AC more thermoplasticity before cure, and higher modulus, tensile strength, and hardness after cure. GR-S-40-AC is being used at present as part of the elastomer in shoe sole and heel and in electrical wire insulating compounds. In the former it smooths out the calender strip from which the uncured blanks are cut and makes it easier to control the weight of the blanks. In wire insulation it increases the rate of extrusion and the surface smoothness of the coating.

X-344-GR-S. This is the non-discolouring, non-staining complement of GR-S-60 intended for use as part of the elastomer in applications in which smooth calendering or extrusion and freedom from shrinkage are required. Applications such as footwear, electrical wire insulation, and hand-made sundries in which surface appearance is important.

Low Water-Absorption Polymers

Coagulated with Acid without Salt

	Polymer composition	Mooney viscosity	Contained acid	Contained stabilizer
GR-S-65 .	76·5% butadiene 23·5% styrene	50	Fatty acid	Discolouring Staining
GR-S-16 .	76·5% butadiene 23·5% styrene	100	Rosin acid	Slightly discolouring Slightly staining

(Mooney large rotor, 4-minute reading, 212° F.)

Coagulated with Alum

	Polymer composition	Mooney viscosity	Contained acid	Contained stabilizer
GR-S-AC .	76·5% butadiene 23·5% styrene	55	Rosin acid	Discolouring Staining
GR-S-10-AC	76·5% butadiene 23·5% styrene	55	Fatty acid	Discolouring Staining
GR-S-45-AC	76·5% butadiene 23·5% styrene	45	Fatty acid	Non-discolouring Non-staining
GR-S-40-AC	58% butadiene 42% styrene	45	Fatty acid	Non-discolouring Non-staining

(Mooney large rotor, 4-minute reading, 212° F.)

Salt and acid are the coagulants used in the preparation of Standard GR-S. Since this technique of finishing unavoidably leaves about 0·2 per cent. soap and 0·9 per cent. ash in the polymer it is not satisfactory for the finishing of polymer used in electrical wire insulation, in steam hose and in some types of water hose, in hydraulic packings, in tank linings and other products in which freedom from electrolytes or water-absorbent matter is necessary for good performance in service.

GR-S-65. This was developed to meet these requirements without losing any of the good characteristics of salt-acid coagulated polymer. It is essentially Standard GR-S low in electrolyte and soluble soap. It is coagulated from standard latex by a special technique and leached before drying to eliminate much of the electrolyte resulting from conversion of the soap. Soap content of GR-S-65 is close to zero, and electrolyte content is less than one-fifth that in Standard GR-S.

TABLE 119. PROPERTIES OF LOW WATER-ABSORPTION POLYMERS

Water Absorption

	Soluble soap content	Total ash content	Water absorption * uncured polymer 20 hrs. 158° F.
GR-S-65	0·02%	0·16%	1·25 mg./sq. cm.
GR-S-AC	0% †	0·57%	2·41 mg./sq. cm.
Std. GR-S, Naugatuck	0·21%	0·40%	4·13 mg./sq. cm.
Std. GR-S, sources other than Naugatuck	0·21%	0·92%	5·13 mg./sq. cm.

* Test made according to Rubber Reserve specification for wire and cable industry polymer.

† Soap in GR-S-AC is an aluminium soap which is not soluble.

Water Absorption during Prolonged Immersion at 158° F.

	3 days' immersion uncured polymer	50 days' immersion uncured polymer
GR-S-65	2 mg./sq. cm.	10 mg./sq. cm.
GR-S-AC	3 mg./sq. cm.	16 mg./sq. cm.
Rubber, smoked sheet	4 mg./sq. cm.	20 mg./sq. cm.
Std. GR-S, Naugatuck	7 mg./sq. cm.	24 mg./sq. cm.
Std. GR-S, other sources	10 mg./sq. cm.	38 mg./sq. cm.

Corresponding Electrical Data

	SIC Original value	% gain 1 day to 14 days	% gain 7 days to 14 days
GR-S-65	4·97	4·4%	2·2%
Std. GR-S, Naugatuck	5·24	3·8%	1·9%
Specification limits for R.W. code	6·0	10% maximum	3% maximum

Insulation Value

Megohms/100 Feet of R.W. Building Wire

	Immersed 2 weeks at room temperature	Immersed 2 weeks in hot water
GR-S-65	11,000	1,200
Std. GR-S, Naugatuck	2,500	600

GR-S-65 insulation is four times as good if comparison is made at room temperature and twice as good if comparison is made at elevated temperatures.

TABLE 120. POWER FACTOR STABILITY

14 A.W.G. Copper Conductor 3/64 Conductor Insulation Difference between percentage of PF at 80 Volts/Mil. and at 40 Volts/Mil.

	1 day's immersion	7 days' immersion	28 days' immersion
GR-S-65	0·66	0·83	0·91
GR-S-AC	0·92	1·00	1·34
Std. GR-S, Naugatuck	1·88	2·03	3·25

GR-S-16. This is coagulated by subsurface atomization of the latex in dilute sulphuric acid and leached before drying to remove most of the electrolyte remaining from conversion of the soap. The water-soluble matter in acid flocculated GR-S-16 is in the range of 0·2 per cent., which is low enough to be satisfactory for pressure-sensitive tapes used on electrical equipment.

GR-S-AC. Because it is low in electrolyte and soluble soap content GR-S-AC also finds some use in electrical wire and cable insulation steam hose, and other applications in which contained water-absorbent matter may lead to premature failure in service.

GR-S-10-AC. Alum coagulated rosin polymer is available under the designation GR-S-10-AC for compounders wanting the characteristics of both the rosin polymer and alum coagulation.

GR-S-40-AC. This is also one of the alum polymers of necessity. It is advantageous in—

1. In adhesives and in combining compounds GR-S-40-AC gives increased film strength.
2. In shoe sole and heel, and in wire insulating compounds it gives smoother calendering, smoother extrusion, higher modulus and tensile strength, and increased cured hardness.

SUPER-PROCESSING POLYMERS

	Polymer composition	Mooney viscosity	Contained acid	Contained stabilizer
GR-S-60	76·25% butadiene 23·25% styrene 0·50% crosslink	55	Fatty acid	Discolouring
X-344	76·25% butadiene 23·25% styrene 0·50% crosslink	55	Fatty acid	Non-discolouring Non-staining

(Mooney large rotor, 4-minute reading, 212° F.)

GR-S-60. The poor processability or more specifically the nerviness of GR-S has long been recognized as one of its shortcomings. Calendered sheets and extruded ribbons of either raw or compounded GR-S are rough in surface appearance and tend to shrink after they have been formed.

These defects may be masked by compounding the polymer with large quantities of filler and plasticizer. Usually this impairs properties important in the fabrication or performance of the finished product. GR-S-60 is the outstanding new development which has overcome these deficiencies. It is essentially standard GR-S to which a small quantity of a cross-linking agent (divinyl benzene) has been added during polymerization. This addition greatly reduces the nerve in the polymer and makes it possible to compound with normal quantities of filler and plasticizer. GR-S-60 is purposely made with more cross-linking agent than is required for the average compound to give latitude to the compounders in several branches of the industry. It is recommended that it be used as part of the elastomer rather than as all of the elastomer unless a high degree of surface smoothness and freedom from shrinkage are required. Some reduction of sulphur and accelerator is usually necessary if the GR-S-60 is used for a large part of the elastomer. The superior processing characteristics of GR-S-60 permit the use of more strongly reinforcing fillers and/or higher viscosity with attendant improvements in finished product quality. It also permits reduction in Banbury or Plasticator mastication since the function of that operation is largely one of improving processability.

When compared to Standard GR-S, GR-S-60 and its blends with GR-S exhibit:

1. Greatly reduced shrinkage (lower than natural rubber).
2. Reduced swelling at extrusion dies.
3. Improved surface appearance.
4. Improved retention of physical properties for aged vulcanizates.
5. Improved physical properties with reduced sulphur acceleration in non-black receipts.
6. Faster curing tendencies.
7. Cooler extrusion characteristics.
8. Reduced requirements for Banbury or plasticator mastication.

GR-S-60 compounds have lower tensile strength and elongation and higher flex crack growth than similar GR-S compounds. These properties may be improved by judiciously blending GR-S-60 with standard GR-S or special-purpose GR-S copolymers. Specific properties are illustrated as follows:

TABLE 121. PROPERTIES OF GR-S-60

	Carbon Black			Mineral		
GR-S	100	50	—	100	50	—
GR-S-60	—	50	100	—	50	100
Tensile lbs./in.²	2,790	2,050	1,700	1,100	870	500
Retention after 96 hrs. at 212° F. (%)	61·3	73·1	82·3	96·5	120	197
Elongation (%)	635	465	355	1,225	890	625
Retention after 96 hrs. at 212° F. (%)	23·6	26·9	28·2	20·8	20·3	26·0
Flex crack growth mils./kilocycle	1·4	5·6	11·7	0·2	2·4	11·7
Heat build-up (Goodrich Flexometer) ° F.	77	70	51	134	76	—
Resilience (%), room temp.	37	36	36	43	42	40
,, (%), 212° F.	45	48	52	53	57	61
Calender rugosity	0·15	0·05	0·05	0·23	0·09	0·04
Calender shrinkage (%)	43	22	9	45	28	3
Swell at Die (%)	54	31	15	58	38	20

(A non-staining variation of GR-S-60 has been developed as X-344-GR-S.)

GR-S-60 is being used in footwear, wire insulation, hard rubber products, coated fabrics, and mechanical goods, including extruded, calendered and moulded types, as well as a processing aid in blends with GR-S and special purpose GR-S copolymer for many rubber products.

X-344-GR-S. This is GR-S-60 made available in a non-discolouring, non-staining form. Properties other than colour stability parallel those of GR-S-60.

MASTERBATCHES OF BLACKS

	Ration of filler/polymer	Filler	Polymer
Black 1	50/100	EPC black	Std. GR-S except 40 Mooney
X-377	50/100	EPC black	4 : 1 mixture GR-S-10 and Std. GR-S of 0·35 Mooney viscosity
X-334	50/100	HMF black	Same polymer as in X-337
X-335	25/100	HMF black	Same polymer as in X-337
X-336	40/100	SRF black	Same polymer as in X-337

Black-1-GR-S. This is produced only by the General Tyre and Rubber Co., Baytown, Tex., plant at the present time. Present production of masterbatch is about 10,000,000 lbs./month. The following advantages have been found to be gained through its use in passenger-tyre-tread compound:

1. Reduced mixing time which increases Banbury capacity approximately 50 per cent. if comparison is made with Banbury mixes compounded with plasticated or premasticated GR-S. If comparison is made with unpremasticated GR-S, the saving is greater.
2. 5–10 per cent. better wear resistance.
3. Better crack-growth resistance which may be retained or converted to improve tread wear by compounded changes.
4. Lower compound cost as indicated below:

	Banbury mixed	Black-1-GR-S
GR-S $\frac{2}{3}$ lb. at 18.5 c.	\$0·1233	\$0·1467
EPC Black $\frac{1}{3}$ lb. at 5.5 c.	0·01833	
Transportation of GR-S	0·00333	·0050
Transportation of black	0·00443	
Plasticating and mixing labour	0·00163	—
Plasticating and mixing power	0·00200	—
Masterbatch cost	\$0·1530	\$0·1517

5. An incidental effect of the use of Black-1 is the increased cleanliness of the mixing department resulting from the part or complete elimination of loose black.

X-337-GR-S. This is a masterbatch of EPC Black in a 4 : 1 blend of rosin acid and fatty acid polymers having a Mooney viscosity of 35 before compounding with black. X-337-GR-S offers the advantages of better wear resistance and better crack-growth resistance.

Preliminary results on tyres indicate wear resistance to be 5–10 per cent. higher than that obtained with Black-1-GR-S and 10–15 per cent. higher than that obtainable with Banbury mixed masterbatch. Crack-growth resistance is slightly higher for the X-337-GR-S compound than for the compounds made with Black-1-GR-S or with Banbury mixed masterbatch. X-337-GR-S also gives the advantages of lower compound cost and increased Banbury capacity. Increased millroom cleanliness and better working conditions also follow from the use of X-337-GR-S.

GR-S Latices (Butadiene-Styrene Copolymers). GR-S latices became generally available in this country in 1944 and 1945, although they had been known and used abroad for several years. The first types were not made up especially for latex use, but were latices from the regular production of GR-S rubber before the coagulation step. Later types were made up especially for use as latex. Although GR-S latices have been available for such a short time, the scale of application is already tremendous, being of the order of 25,000 tons per year.

GR-S Latex, Type I. Type I, GR-S latex is the emulsion of polymerized butadiene and styrene made as a step in the production of GR-S synthetic rubber. The polymer, therefore, has a butadiene-styrene ratio of about 75 : 25 and contains an antioxidant of the staining type.

This latex is emulsified with fatty acid soap and has a total solids of about 27 per cent. The particles are in the range of 0·07 micron in diameter, and because of their small size are in Brownian motion and do not cream even though the gravity of the particles is low (0·94). The particles are negatively charged, and the latex lends itself therefore to compounding with the same type of dispersion as used with *Hevea* latex.

Type I latex forms very weak gels and films which have a tendency to crack during drying. Because of these properties its application in latex processes has been very limited. Films of Type I latex have in general the properties of milled GR-S pure gum films. They are dark in colour, show slow tensile and tear strength, are slow drying, and have high water absorption. They also have good low-temperature properties and ageing properties and poor solvent resistance.

Type I latex stocks are slightly lower in cure rate than *Hevea*, but lend themselves satisfactorily to ultra-acceleration and low temperature cures. Although reinforcement of latex stocks with colloidal materials is generally not considered feasible, a definite reinforcement of Type I latex stock has been indicated by use of certain carbon blacks and fine organic and inorganic pigments.

Because of the low physical properties of its films, Type I latex has not found wide application in latex processes. Thus far it has found some application in tyre cord dips, fibre binding, and impregnation.

GR-S Latex, Type II. Type II latex differs from Type I only in that the antioxidant has been omitted, thus allowing the compounder to select the best one for his own particular need. Because of the elimination of the staining type of antioxidant, Type II films are light in colour; otherwise its properties are the same as those of Type I latex.

GR-S Latex, Type III. Type III was produced specifically as a latex for general-purpose use and shows many advantages over the other types. In Type III latex the butadiene-styrene has been increased to a 50 : 50 ratio; the emulsifier has been changed to a rosin soap, and the polymerization has been carried to a higher state. The gels and film strength of Type III latex are greatly improved. This latex lends itself to a much wider field of application than the others and has in many ways served as a general-purpose latex.

Type III is a stable emulsion of butadiene-styrene having a total solids content of approximately 38 per cent. Its particles are negatively charged, and because of their small size (0·07 micron) show Brownian motion and little tendency to cream. This type can be handled by methods common to latex practice. It lends itself readily to concentration by creaming or evaporation. Creams using ammonium alginate-type of creaming agent are available at greater than 50 per cent. total solids, while evaporated concentrates above 50 per cent. total solids are available commercially.

Type III latex films are light in colour and, when properly compounded, have good age resistance. They stiffen markedly at low temperatures and show decreased tensile and tear strength at elevated temperatures. Films are relatively slow-drying and high in water absorption.

Type III films require the same general type of compounding for cure as *Hevea*. As some of the ultra-accelerators function satisfactorily in Type III, this latex lends itself to low-temperature fast cures generally used in latex processes. Thickeners, softeners, stabilizers, and fillers perform, in general, the same function as with *Hevea*.

Among the many applications of Type III latex are cord dips, for tyres or belting, adhesives, paper and fabric saturants, curled hair-binders, coatings, can-sealing, rug and fabric backings, and dipped goods.

Comparison of Natural Rubber and GR-S (Latex) Films. Here are some interesting comparative figures for natural rubber (creamed) latex having a minimum age of four years and GR-S latex, Type II and Type III respectively, in the form of vulcanized films:

TABLE 122. PROPERTIES OF GR-S FILMS

Property	GR-S Type II	GR-S Type III	Natural latex
Time of cure (min./300° F.)	45	45	20
Tensile strength (lb./in.^{2})	350	1,250	3,500
Elongation, per cent.	325	360	850
Hardness (Shore A)	47	50	40
Goodrich Flexometer: Temp. rise — ° F. above 100° F.	73	64	12
Blow-out time-minutes	4·5	9·5	over 1 hr.
Comp. set per cent.	15·3	17·7	1·4
Oven-ageing, 24 hrs./212° F.: Tensile strength (lbs./in.^{2})	500	900	3,900
Elongation, per cent.	290	330	750

Low Temperature Rubbers. The most exciting development in the synthetic rubber field is the production of "low temperature rubber". This refers to copolymerization of butadiene and styrene

at low temperatures. The usual temperature for making GR-S is 122° F. Temperatures used for low-temperature rubber are 41°, 14°, and 0° F. and lower. If polymerization at low temperature is carried out in the ordinary way the process is very lengthy owing to the slowing-down reaction. Polymerization at low temperature has been facilitated by the introduction of Redox methods (see page 225).

The leading low-temperature rubber at the present time are Philprene A and B, made by the Philprene Corporation, and Ultipara, made by the Copolymer Corporation. Other types are on the way.

A typical large-scale reactor charge is as follows: [4]

Styrene	317 gallons
Butadiene	1,110 ,,
Activator	130 ,,
Soap	663 ,,
Water	1,030 ,,
Modifier	15 to 18 lbs.
Cumene hydroperoxide	12 to 15 lbs.

This is processed for 20 hours at 41° F., compared with a normal GR-S reaction period of 14 hours at 122° F.

Tyre treads based on Philprene A have been shown to be up to 40 per cent. better than similar treads based on GR-S 10 in most physical properties.[3] In particular they show excellent resistance to cut growth and cracking. They are also superior to natural rubber treads.

Philprene B made at lower temperatures still, 14° F., have also shown excellent physical properties.

Ultipara, made by the Copolymer Corporation at Baton Rouge, is claimed to be superior to natural rubber in all major respects even in applications such as car tyres and heavy-duty tyres.

It seems already clear that low-temperature polymerization yields rubbers which are very much improved in essential properties compared with those made at higher temperatures. While it is still early it would nevertheless seem that low-temperature polymerization represents a very great step forward. It would seem to be the greatest advance in closing the gap between the properties of synthetic rubbers and natural rubber.

REFERENCES

[1] BRADY, *India Rubber World*, 1947, **115**, 509.
[2] HUCKS, *Ibid.*, 1947, **115**, 347.
[3] SCHULZE, REYNOLDS, FRYLING, SPERBERG and TROYAN, *Ibid.*, 1948, **117**, 739.
[4] SHEARON, MCKENZIE and SAMUELS, *Ind. Eng. Chem.*, 1948, **40**, 769.

CHAPTER 15

ELASTOMERS—BUNA-S

THE German manufacture of synthetic rubber was on a very large scale, mounting steadily in the years before the war. The actual figures were:

1938	5,000 tons	1942	96,000 tons
1939	14,000 ,,	1943	115,000 ,,
1940	40,500 ,,	1944	101,000 ,,
1941	68,000 ,,		

The main production was for a number of years, until 1942, Buna-S based on butadiene and styrene. It was superseded by Buna-S3 which had superior tackiness and adhesion and which became standard material for tyres. The main difference was in the emulsifying agent used for polymerization. The following account describes how Buna-S3 was actually synthesized at Schkopau.

The composition of the emulsion for making Buna-S3 was:

	Parts by weight
Butadiene	70·0
Styrene	30·0
Nekal (sodium isobutyl naphthalene sulphonate)	3·0
Sodium paraffinate	0·5
Sodium hydroxide	0·4
Potassium persulphate	0·4
Diisopropyl xanthogenate (diproxid)	0·1
Water	106

The degree of conversion was about 55–60 per cent.

In addition to these Buna-SS was made, chiefly for extrusion purposes and for cables. It consisted of 46 parts butadiene and 54 parts styrene. It was much easier to process than Buna-S or Buna-S3. While tensile strength was higher, elongation and low temperature resistance were inferior. Conversion was carried to 55 per cent. and the Defo number was about 3700.

Buna-S3. Buna-S3 is made at Schkopau[5] using a continuous polymerization process with 10 or 12 reactors connected in series. One building has four lines each with twelve reactors—a total of 48 reactors, each 12 cubic metres in volume. This building has a capacity of 3000 tons/month Buna-S3 (half the plant capacity) or 3500 tons Buna-S. There are two other buildings.

The entire process is continuous except for the making up of Nekal and fatty acid and sodium salt solutions, the preparation of the persulphate solution, and the preparation of the diproxid solution in styrene.

Butadiene is received from the Butadiene manufacturing department and is stored in underground tanks. It has a purity of 98·5 per

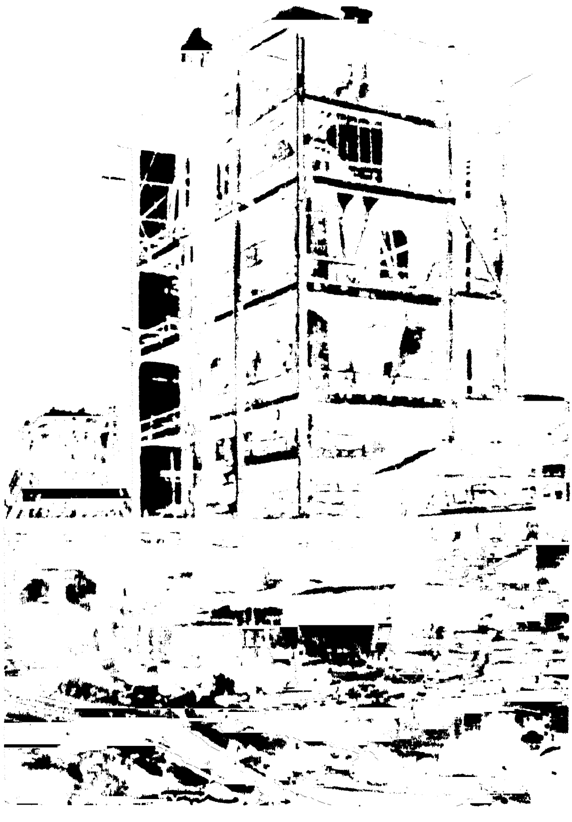


FIG. 74.—Part of the Buna Plant at Schkopau.

cent., or better, and usually around 99 per cent. The product is quite dry as is the styrene.

The Buna-S3 Department storage tanks for both butadiene and styrene are underground, the butadiene tanks are iron and the styrene tanks are aluminium. Before installing the underground tanks they were covered with a special felted textile material and heavily coated with tar.

Butadiene and styrene are pumped from the underground tanks using a special type of three-stage centrifugal pump which has good suction and raises butadiene or styrene out of the tanks up to the pump. The correct amount of butadiene and styrene are pumped into a vertical mixing tank (each tank has a capacity of 40 cubic metres, and is filled to 33 cubic metre content, which is 20 tons butadiene).

FIG. 75.—One of the Units for preparing the Polymers at the Schkopau Works.

The contents of the tank are circulated by one of the centrifugal pumps to give a complete blend of the monomers. There are three blending-tanks for each Buna-S building.

The mixture of the hydrocarbons is pumped from the blending tank through an indicating meter to a premixer. This is a vessel of 5 cubic metre content and is filled to $3\frac{1}{2}$ metres. The hydrocarbon mixture and the Nekal-fatty acid solution are emulsified in this vessel,

which is continuous in operation. The mixer vessel and most of the main lines, the valves, polymerizers, persulphate dissolver, pump and all lines, are made of V_2A metal (18 copper, 8 nickel). A stream of Nekal and soap solution (already mixed) enters continuously into the premixer and leaves continuously.

The specific gravity of the hydrocarbon mixture going from the blend tank to the premixer is continuously indicated and recorded by a specific gravity meter. This appears to be an excellent way to check the monomer ratios as there is a considerable difference between the specific gravity of butadiene and styrene. If the specific gravity is within the correct limits no other tests appear to be made to check the monomer ratio.

The Nekal soap solution is prepared in a solution building adjacent to the Nekal plant. The Nekal comes into the solution building by pipe line as a 17 per cent. solution.

The fatty acid comes in aluminium tank cars from Oppau, where it is produced by the oxidation of paraffins and is stored at Schkopau in aluminium tanks. The synthetic fatty acid and the caustic soda liquor charged are weighed in on scale tanks. Water is added after first being treated with lime ($Ca(OH)_2$) to remove $CaHCO_3$, then the water is passed through a synthetic Zeolite to change soluble lime salts to soda salts. The neutralizing tanks are large steel tanks, which are rubber lined. Nekal is added and the tank contents adjusted to the correct water concentration for charging to the Buna-S3 polymerizers. The tank contents are transferred batchwise—a tank at a time to any one of the three polymerization buildings.

The Nekal goes to the premixer as a 3 per cent. solution, Nekal being calculated as the pure sodium salt of the Butyl naphthalene sulfonic acid. 4·5 parts of Nekal and 3 parts of fatty acid are used per 100 parts of Buna-S3.

The phenyl-β-naphthylamine emulsion is also made up in the solution building for the entire Buna-S3 plant. Phenyl-β-naphthylamine is charged into the manhole of a steel steam-jacketed kettle with a stirrer; then the manhole cover is put on and the material is melted. There is a well-ventilated hood over the manhole opening connected to a suction fan. The molten PBN is dropped through steam-jacketed lines into a steam-jacketed measuring tank, then fed through a jacketed line to the suction feed opening of a centrifugal pump (the line is jacketed right up to the pump casing), where the PBN is mixed with water containing 1 per cent. Nekal (20 parts PBN—80 parts Nekal solution), and then run into a homogenizer running at 3000 r.p.m. The resulting PBN emulsion is quite stable and is transferred in batches

to any one of the three Buna-S3 buildings. The emulsion is also measured from the storage tank in each building to the measuring tanks which feed each polymerization line.

The Nekal fatty acid soap mixture is emulsified with the hydrocarbons in the premixer by a paddle agitator running between 25 to 30 r.p.m.—very moderate agitation. One premixer supplies an entire Buna-S3 building (4 lines of 12 reactors each). Another premixer is available as stand-by. The monomer and Nekal soap solution are heated on the way to the premixer to 40° C. at which temperature the premixer contents are maintained. The emulsion of hydrocarbons, Nekal and soap, are continuously pumped by a centrifugal pump from the premixer to a pressure header which supplies the four Buna-S3 lines. The rate of flow of emulsion to each line of reactors is hand controlled from this line with an indicating meter to show the operator the rate of flow at all times. The emulsion goes into the first reactor of each line through a line extending to the bottom of the first reactor and overflows from the top, the reactor being completely full of liquid with no gas cushion.

The polymerizers in the building under discussion were " plated " with V-2A steel (chrome-nickel steel). Schkopau uses both enamelled and lead-lined (homogenous-lined) polymerizers. They prefer the V-2A lined vessels as it gives better heat transfer than enamel and less cleaning than the lead-lined vessels.

The polymerizers are of two sizes. In one building they are 12 cubic metres capacity and the stirrer speed is 58 r.p.m. In the other building they are of 20 cubic metres capacity with a stirrer speed of 25–30 r.p.m. The stirrers are of two kinds. One has two horizontal paddles (some have only two horizontal paddles), and in the other the stirrer is constructed in the form of an elipse. The agitation with both stirrers is quite moderate. The temperature of the reactors is maintained between 45° and 48° C. If the temperature goes much above 50° C. dimerization is said to take place forming vinyl cyclohexene. This butadiene dimer is stated to be objectionable in Buna-S3, particularly with regard to the subsequent heat treatment. It is also stated to give a strong odour to the rubber.

The average reaction time for the butadiene reactors is stated to be 30 hours. However, the effect becomes quite small after eight or nine reactors, and at Schkopau they did not think that there was any perceptible difference in the rubber made in nine polymerizers compared with twelve polymerizers. However, the fewer the reactors in the chain, the greater the disturbance to the process when one reactor is taken off for cleaning. Schkopau prefer to operate all lines with

twelve or eleven reactors with one reactor out of service. Conversion is carried to 58–60 per cent. The control of the polymerization to this conversion is normally done by adjusting the temperature of the polymerizers. This is done by hand control, the temperature is raised or lowered for the entire line, and this method of control is stated to be entirely satisfactory. The flow rate is normally maintained at a constant rate. If due to a change of the quality of butadiene, or other materials charged, and a considerable change in polymerization rate should occur, the flow rate would then be changed. The temperature is maintained within three degrees (45°–48° C.).

The potassium persulphate solution is made up in a solution tank from which it is charged to a feed tank and pumped into the first reactor by hand control. The tank has a side glass and movable tabs are used which the operators set to show what the level should be for each hour ahead. This is a very simple method and is said to give entirely satisfactory control.

The diproxid feed tank and pumping unit is movable and can be attached to any reactor. It has a special single-stroke pump which discharges into the reactor to which the unit is attached. The diproxid is first made up as a 5 per cent. solution in styrene. The diproxid goes into three vessels, being introduced where the conversion is as shown below:

	%
1st	12
2nd	30
3rd	45

By introducing the diproxid in this way, it is stated that a polymer of constant viscosity is formed throughout the polymerization.

The reason for making the diproxid portable is because the number of the kettle where diproxid should be added will vary sometimes, particularly depending on whether there is eleven or twelve working reactors.

The PBN emulsion, which is added to stop the reaction, is introduced when the latex leaves the last reactor. The reaction is not completely stopped by the PBN used. To stop the reaction completely, it would be necessary to use bisulphite ($NaHSO_3$) to destroy the persulphate completely.

The pressure in the first polymerizer is maintained between 7½ and 8 atmospheres. The pressure has dropped to about 6 atmospheres when the latex has left the twelfth reactor and is entering the filter. The pressure upon leaving the filter is 5 atmospheres, but goes down to 4 atmospheres when the filter is full.

The latex filters are enclosed leaf filters, each line having one filter unit in operation and one spare filter unit. The filters are 1 metre in diameter and 2·2 metres long. Each filter contains 4 leaves, each about 30 cm. high, 2 metres long. The total filter surface in each filter is stated to be about 5 square metres, and the filter surface is metal screen with mesh 2 mm. × 2 mm. The filtered latex then goes to the stripping unit.

Latex Stripping. The latex is stripped of any unreacted gases by mixing latex with a mixture of steam and hot water venting into a large vertical cylindrical tower containing horizontal baffles sloping downwards. The latex and steam are separated in this unit, the outlet at the bottom of the tower being cone shaped and the size of the opening being manually controlled by a valve. There is a sight glass in the outlet from the vertical tower in the horizontal tank below through which the operator looks to determine whether any latex foam is going out with the gases. The partially stripped latex is pumped into a similar type tower with more steam and the latex and vapour again separated. The gases then go through a condenser where the temperature is so controlled that only water separates out, and the mixture of butadiene, steam, and styrene is gaseous. The water condenser is quite large, 140 cm. in diameter and 3 metres long, comprising 1100 20-mm. tubes.

The gases then go through a second condenser cooled with refrigerated water where the liquid styrene condenses out. The butadiene gas then goes to a compressor where it is compressed, and subsequently cooled, whereupon the butadiene condenses to a liquid. There are two stripping batteries for each polymerization line—one working and one spare.

The crude styrene obtained is practically free from coagulum and is distilled in vacuum in a single-still unit that looks like a single-effect evaporator (two vapour-heating units and one still body). The redistilled styrene is stated to be 99·2 per cent. pure. It is returned to the charging system, mixed with fresh styrene, and is charged to the polymerization line.

Recovered butadiene is also returned to the charging system and blended with the fresh monomer.

The stripped latex goes continuously into a storage tank and continuously out of the same tank through a pipe-line to another building where it is coagulated. The stripped latex storage tank has a volume of 30 cubic metres and has a horizontal stirrer to keep the PBN from settling out. There is no attempt at blending. It is considered that the material is homogenous and the properties

well controlled and uniform when the latex leaves the last reactor.

Coagulation. At the coagulation plant there are three storage vessels, each 30 cubic metre capacity vertical tanks. These tanks are out of doors but insulated (to prevent freezing). The purpose of having three storage tanks is to have a small cushion in case operation in either the coagulation plant or polymerization plant were interrupted for a short time. Normally, latex flows continuously in and out of the same tank, and no attempt is made to blend the latex. Pipe coagulation is used, the unit being extremely simple. (Pipe is 50 mm. in diameter—about 2 inches and made of polyvinyl chloride (Igelit). The coagulation unit is located right above the control board.

Latex is mixed with three materials in two mixing stages. In the first stage, calcium chloride is added. In the second stage, acetic acid and water is added. Calcium chloride and acetic acid are introduced in such a way to give tangential flow. It was subsequently stated at Ludwigshafen that coagulation of Buna-S3 could not always be effected by calcium chloride alone and sometimes sodium chloride had to be added also. When calcium chloride only was used, at times the wet Buna-S3 band had insufficient strength and broke on the Foudrinier machine.

The coagulated latex is then passed through a Foudrinier (paper machine). This unit is 17 or 18 metres long and about 2·2 metres wide. There are two coagulation buildings, and there are four Foudrinier units in the larger building. These four units can produce 3500 tons of Buna-S3 per month.

The sheet is formed in the usual way with vacuum and washed as is done with paper. The wet sheet finally passes through two large squeeze rolls, 18 inches in diameter. As it comes out of this machine the sheet contains 48 to 52 per cent. of Buna-S3. The material then goes through a hot air drier with seventeen passes in the heating zone and two passes in the cooling zone. The temperature is maintained at 115° to 117° C. at the top, 110° C. in the middle of the drier, and 105° C. at the bottom. The sheet is cooled to 30° C. in the cooling zone. The sheet from the drier is finally powdered with talc and rolled into 100-kg. batches.

Schkopau has another drying unit where the sheet from the Foudrinier is passed through a hammer mill, and the crumb then passed through a de-watering press. The wet material is forced through by hydraulic pressure and water filters out from the crumb. Three presses are used for one crumb drier. The material entering the press is about 66 per cent. of water, 33 per cent. of Buna-S3. On

leaving the press it contains only 25 per cent. of moisture. The crumb is disintegrated in another hammer mill and fed into a hot air continuous drier, 37 metres long, 3 metres wide, and 3 metres high. Air is circulated through the material on a screen belt, the drying temperature being maintained at 75° C. In the last zone the Buna-S3 crumb is cooled to 35° C. (using air at a temperature of 20° C.). Buna-S3 comes out of this unit with a moisture content of less than 0·5 per cent.

Production at Hüls[6] was much along the same lines. They had made four types of Buna rubbers—Buna-S, Buna-SS, Buna-SR and Buna-S3. Polymerization was carried out as a continuous process in eight lines of six reactors. The mixture was pumped continuously through five reactors (leaving one spare) at about 45° C. Reaction was carried to about 60 per cent. and took about 30 hours.

In the case of Buna-SR, the temperature in the sixth reactor was kept at 80°–90° C., and a conversion of 96 per cent. was attained. Rate of production was about 1 ton per hour.

Buna type	Percentage conversion in each reactor				
	1	2	3	4	5
S	20	35	44	52	57
SS	20	36	45	54	60
SR	15	25	32	40	95
S3	20	35	44	52	57

The change from Buna-S to Buna-S3 resulted in much improved properties. Among the advantages were better mixing, lower power requirements, superior tack and adhesion, while vulcanized products were very satisfactory. Whereas the Defo number of Buna-S was 4300, the Defo number of Buna-S3 was down to 3000, i.e. it was much softer.

Apart from the solid types, Buna-S and Buna-S3 materials have been available as latices. Igetex-S is the latex of Buna-S available in a 35 per cent. solid content and also a 45 per cent. solid content. Igetex-SS was the latex of butadiene 57 parts, styrene 43 parts, and was available as a 45 per cent. solid content latex.

Koresin.[7] This is the outstanding tackifying agent made at Ludwigshafen by reacting acetylene with paratertiary butyl phenol derived from isobutylene and phenol. Koresin is an extremely effective

tackifying agent. According to the Germans, if it were not used, then at least 15 per cent. natural rubber had to be added, especially in tyre mixes.

Isobutylene was introduced continuously into a porcelain-lined jacketed autoclave, fitted with a stirrer, and containing phenol. A temperature of 50° C. and 5 atmospheres pressure were maintained. Anhydrous aluminium chloride and phenol were added continuously mol for mol. The product was withdrawn continuously from the bottom, was neutralized, washed and decanted continuously. The crude product was batch distilled at atmospheric pressure. Phenol was recycled and the fraction distilling between 92° and 95° C. was the paratertiary butyl phenol of 95 per cent. purity used in the next step.

In the next step 800 kg. of isobutyl phenol and 70 kg. of zinc naphthenate were melted and mixed in a jacketed stirred kettle at 90° C. and introduced under nitrogen pressure into a heavy horizontal cylindrical autoclave of 1·5 cubic metres capacity which had been previously purged with nitrogen. This autoclave was fitted with a stirrer consisting of a horizontal shaft rotating at 35 r.p.m. having a number of straight projecting arms. It was surrounded by a high-pressure steam-jacket.

The contents were heated to 180° C. by 20 atmospheres steam pressure in the jacket. Nitrogen was added to 3 atmospheres pressure. After discontinuing heating, acetylene was introduced at a rate sufficient to increase the temperature to 230° C. but not above 240° C., maintaining pressure at 20 atmospheres.

Reaction time was 8 hours, total cycle 12 hours, 1·3–1·5 mols of acetylene were absorbed per mol of phenol. Theoretical consumption of acetylene was 165 cubic metres, but actual consumption as measured by the metre in the plant was usually 180 cubic metres. Addition of too much acetylene prevented removal of the product from the autoclave.

Towards the end of the reaction samples of product were taken and the melting-point determined in an Ubbelohde instrument. When this reached 135° C. the product was discharged to an open stirred kettle to remove acetylene and nitrogen.

Smith, Ambelang and Gottschalk [3] have described the preparation and properties of numerous alkylphenol resins in the United States.

Buna-S, unless previously treated, is somewhat difficult to process. It requires a special technique to break it down to a plastic condition. Although Buna-S had been developed as long ago as 1928, yet ten years elapsed before a practicable method for handling it was developed.

It has been plasticized by means of hot air. The process was carried out on the largest possible scale in Germany.

On the other hand, the newer types such as Buna-S3 offer much less difficulty in processing. Improvements in this respect are being made all the time, so that thermal degradation is no longer universally practised. It is, however, worth consideration as an indication of the difficulties encountered.

Thermal Degradation of Buna-S. One of the most important problems that had to be met before Buna-S could be used on an adequate scale was to overcome the stiffness which makes it so hard to process. It can be softened by prolonged mastication in up-to-date mills, but this action consumes too much time and power. The addition of appropriate plasticizers in the required amounts had been tried, but this had an injurious effect on the quality of the final product.

In 1937 a method of reducing the molecule of Buna-S was developed by Hagen,[1] which has since become known as thermal degradation or thermal decomposition. This method was predominantly used in Germany, and at one time the fact that Germany was able to use synthetic rubber successfully on a large scale was attributed to this thermal degradation process.

Shredded Buna is spread on racks to a definite, constant thickness; the racks are introduced into degradation ovens where the material is subjected to thermal treatment in the presence of air or oxygen. The main requirements for obtaining a uniform final product are thorough motion of air and uniform temperature distribution in the interior of the oven. In most modern factories special degradation ovens are employed which have the necessary attachment for supplying a stream of heated compressed air.

In recent German manufacture the methods of thermal degradation have been employed by autoclave heating and by a continuous process.

In the autoclave method strips of Buna $\frac{1}{4}$ inch wide were piled on trays and heated in air under pressure. A typical cycle was heating at 135° C. for $\frac{3}{4}$ hour under 5 atmospheres (75 lbs. per square inch) pressure.

The continuous method consisted of passing the material on a conveyor belt through a heated tunnel. Temperature used was 140° C. and the time was about 35 minutes.

By carrying out the thermal degradation the Buna is brought to a workable condition. Thus Buna as delivered to rubber manufacturers had Defo values between 3000 and 5000. For compounding, this had to be reduced to 700–1000, which is achieved by the thermal degradation.

TABLE 123. AGEING OF SOFTENED BUNA-S [4]

	T_B Kg.cm²	E_B %
Room temperature	230	720
Geer oven at 70° C.		
8 days	235	530
16 "	238	510
32 "	240	500
Oxygen bomb at 100° C.		
8 days	234	690
16 "	228	630
32 "	200	560

The chemistry of the degradation process has not yet been explained. It is certain, though, that the presence of oxygen is essential; no softening occurs in nitrogen or steam. A part of the phenyl-β-naphthylamine, which is incorporated as a stabilizer for the Buna prior to marketing, is used up, but what remains normally suffices to give the vulcanizate anti-ageing protection.

When Buna-S is subjected to such treatment, plasticity first increases very rapidly; at the same time the viscosity of a 4 per cent. benzene solution decreases. After reaching a minimum, hardness and viscosity increase again. This minimum may be called the resinification point, for if the thermal treatment is prolonged beyond this point, the adhesive properties of the material progressively decline, the "elastic portion" increases (seriously hampering extrusion and calender work), and, if continued for a long time, a hard, brittle, translucent substance is obtained which is no longer soluble in organic solvents. It is evident, therefore, that after a certain stage of softening has been reached, a cyclization reaction develops.

In softening Buna by this method, care must be taken never to reach the point of resinification. The proper temperature and duration of treatment are thus important. For though a higher temperature increases the rate of softening, the danger of cyclization is also increased; furthermore, too high a temperature and too short a period of treatment prevent the obtaining of a uniform final product. It has been found that heating should be continued for periods of not less than 30 minutes and at a temperature of around 150° C.

The changes that occur on heating have been explained by assuming two reactions. In the early stages of heating there is breakdown of the molecules due to oxygen. This leads to some decline in physical properties after vulcanization. The second reaction has been described as "oxygen vulcanization" or cyclization, and its effect on physical properties is even worse.

The degree of tack attained by thermal treatment is not equal to that obtained by replacing 20 to 30 per cent. of Buna-S by natural rubber. This accounts for the great importance attributed to Koresin.

Advantages and Disadvantages of Thermal Degradation. Thermal treatment of Buna-S offers various advantages—by its aid the power requirements for mixing, time for mixing, and size of pieces treated are on a level with that usual for natural rubber ; hence the mixing process becomes cheaper. With a higher degree of softening a kneading machine can be used for mixing.

Dispersion of fillers is improved, which in some cases increases the strength of the product and always reduces the amount of waste. On the other hand, the vulcanizing ability of the Buna is somewhat decreased, and the mechanical properties are also affected, the impairment depending on the degree of softening. Increased amounts of sulphur and accelerator are needed, and in general much greater care in compounding is essential.

Table 124 shows experimental results on tyre-tread mixes based on Buna-S which has been heat treated compared with untreated material are most illuminating. It is absolutely essential to incorporate a large quantity of plasticizers in order to compound raw Buna-S. In this respect it resembles most other elastomers. But after it has been submitted to heat treatment this is not necessary. It is also interesting to note that in common with other elastomers less sulphur and more accelerator is required than for natural rubber. The mixes were all taken to optimum state of vulcanization.

Although the Germans have had comparatively long experience in handling Buna-S, they have not overcome the processing difficulties. In fact, it appears that their extensive use of Buna-S was geared to their production of reclaim, which was an essential ingredient.

It is clear that the standard range of rubber softeners perform a useful function in Buna-S by aiding the dispersion of the high loadings of blacks. But they do not give that tack which is required for the successful building up of composite articles such as tyres. All these properties have been improved in Buna-S3. In particular tackiness and welding behaviour are far superior.

Thermally softened Buna-S continues to show a greater tendency to shrink than natural rubber having the same plasticity, and it does not give such smooth extruded and calendered products, so that the addition of a certain amount of softener is still necessary. There is a similar difference in the processing qualities of degraded and masticated Buna-S which favours the latter. Subsequent thermal treatment of

TABLE 124. BUNA-S TYRE TREAD MIXES (German)

	Buna-S Untreated	Buna-S Heat softened	Natural rubber
Rubber	100	100	100
Carbon black	42	42	42
Stearic acid	2	2	2
Ozokerite	1·5	1·5	1·5
Sulphur	1·3	2·2	2·6
Vulcacit AZ	1·2	1·2	0·9
Coumarone resin	12	—	—
Rosin	5	—	—
Mineral oil	5	—	—
Caoutchol	5	—	—
Zinc stearate	5	—	—
T_B Kg.cm.^{2}	200	250	280
E_B %	480	600	580
Elasticity %	44	45	50
Shore hardness	73	70	70

masticated Buna does not destroy this advantage, so that thermal treatment of Buna-S is sometimes preceded by brief mastication.

Properties of Buna-S. Buna-S compositions have remarkable ageing characteristics and resistance to heat. The following table illustrates these features. The mix used was Buna-S 100; Carbon

TABLE 125. AGEING OF TREATED TYPICAL TREAD MIX [1]

Ageing-period	Unsoftened, with 1% S T_B	E_B	M_{100}	E	H	Strongly softened, with 2% S T_B	E_B	M_{100}	E	H
Ordinary temperature	225	690	38	54	65	203	670	52	50	68
Geer oven at 70° C.										
8 days	230	540	74	56	72	210	475	106	54	77
16 days	236	525	86	57	75	204	420	121	53	78
32 days	228	510	99	56	76	180	300	141	54	79
Oxygen bomb at 100° C.										
8 days	227	675	54	54	72	198	570	81	52	73
16 days	625	640	61	55	75	196	540	90	51	76
32 days	211	640	67	56	76	180	500	105	53	78

black 42; Stearic acid 2; Ozokerite 1·5; Sulphur 1·2; Vulcacit AZ 1·5. The Buna-S was strongly softened and the mix was carried to optimum cure.

The Germans claimed that Buna-S tyres are considerably better than natural-rubber tyres. According to Stöcklin,[4] on evidence based on road tests, Buna-S tyre tread has an advantage of 35 per cent. over the best type of natural-rubber tread in respect to abrasion resistance.

During the war permeability of materials towards gases and liquids was of more than normal importance. It has, of course, a profound bearing on the moulding characteristics, for one of the important factors is an adequate ability to permit air to pass through. On the other hand it is a disadvantage for applications such as balloon fabric where gas must be retained. In this respect Buna-S allows the passage of rather more air than does rubber.

TABLE 126. AIR PERMEABILITY OF VULCANIZED PURE GUM ELASTOMERS [2]

	$\frac{\text{cm}^3 \text{ air}}{\text{h.cm}^2.\text{cm.mm.Hg}}$	
Rubber	3·4	100%
Buna-S	5·3	156%
Perbunan	0·6	18%

TABLE 127. WATER ABSORPTION

	%
Rubber	6·5
Buna-S	4·5
Buna-SS	6·0
Perbunan	7·5
Perbunan-Extra	7·5

Buna-S is a pure hydrocarbon. As a result it has excellent electrical characteristics and is extensively used both for insulation and protective sheathing of cables. Thus at 20° C. and 50 cycles Buna-S has a dielectric constant of 2·9 and power factor of 0·0007. While resembling rubber in electrical characteristics, it has much better moisture resistance and retains its electrical properties at high operating temperatures for much longer periods of time. It also has good resistance towards ozone.

Table 128. Water Permeability

Mix.	Rubber	100
	Zinc oxide	5
	Sulphur	1
	Vulcacit AZ	1
	Stearic acid	2
	P.33	as indicated

$$\frac{\text{gm. water}}{\text{h.cm.}^2\text{cm.mm.Hg}} \times 10^{-8}$$

	Raw gum	No fillers	Vulcanized mix with 25 parts P.33	Vulcanized mix with 50 parts P.33
Rubber	27	6·2	4·8	4·7
Buna-S	18·6	12·9	9·9	7·8
Buna-SS	8·1	5·1	4·2	3·4
Perbunan	28·1	17·6	15·1	12·6
Perbunan-Extra	21·2	13·6	10·7	9·5

Table 129. Electrical and Mechanical Properties of Buna-S and Buna-SS

	Specific resistance Ohm cm.	Insulation resistance Meg. km.	Insulation resistance After 12 weeks at 100° C.	T_B Kg/cm.²	E_B %	T_B After 1 week in air at 100° C.	E_B After 1 week in air at 100° C.	T_B 12 weeks in air at 100° C.	E_B 12 weeks in air at 100° C.
Natural rubber	20×10^{14}	950	600	103	270	92	220	0	0
Buna-S	7×10^{11}	350	1000	52	320	57	270	52	60
Buna-SS	13×10^{11}	400	4000	88	390	92	340	85	140

Table 130. Typical Heat-resisting Mix

Buna-S	100
Kieselkreide (silica)	60
Softener	3
Antioxidant	3
Thiuram disulphide	2·5
Zinc oxide	2
Sulphur	0·12
Polyacrylic ester	16

Vulcanized from 30 to 60 minutes at 40 lbs. per square inch.

Preparation of a Buna Tread Mix. The preparation of tyre tread rubber was carried out in one of the leading German works along the following lines. The actual tread mix was made up from three master batches.

Main batch	M.7248	88·7 parts by weight
Sulphur master batch	M.6327/2	4·8 ,, ,, ,,
Accelerator master batch	M.6585/4	6·5 ,, ,, ,,

50 kg. were mixed together in 12 minutes on an 84-inch mixing mill.

The composition and treatment of the respective master batches is of considerable interest.

TABLE 131

MAIN BATCH—M.7248

	Parts by weight	Time in internal mixer
Buna-S3 (Defo 700)	50·75	
Buna reclaim	5·65	4 minutes
WA3 (a substituted wool fat)	2·125	4 minutes
PBN	0·54	1 minute
Naftolen	5·3	7 minutes
CK3 Black	32·2	
Zinc oxide	2·05	
Paraffin	1·325	
Aktiplast SB (zinc salt of a synthetic fatty acid)	0·15	7 minutes
Time for removal from mixer		2 minutes
200-kg. batch took		25 minutes

SULPHUR MASTER BATCH—M.6327/2

	Parts by weight
Buna-S3 (Defo 700)	60
Zinc oxide	10
Naftolen ZD	5
Sulphur	25

60-kg. batch took 40 minutes on an 84-inch mill.

ACCELERATOR MASTER BATCH—M.6585/4

	Parts by weight
Buna-S3 (Defo 500)	77
Zinc oxide	10
Aktiplast SB	2·9
Aniline Red	0·1
Vulkacit DM (benzthiazyl disulphide)	10

50-kg. batch mixed in 30 minutes on an 84-inch mill.

TABLE 132. STANDARD BUNA-S COMPOUND FOR EXTRUDED ARTICLES

Buna-S (Defo 1000)	100	100
ZnO	5	5
S	2·2	2·2
Vulkacit AZ	1·8	1·8
PBN	1·5	1·5
Paraffin	1·5	1·5
Black P.1250	30	30
Lamp black	30	75
Factice	10	20
Plastikator 88	40	15
Naftolen ZD	10	—
Cure: 30 minutes at 150° C.		
S.G.	1·14	1·16
Shore hardness	45	70
T_B kg. per sq. cm.	75	109
E_B, %	495	310
Schopper elasticity, %	58	56

TABLE 133. STANDARD BUNA-S COMPOUND FOR MOULDED ARTICLES

Buna-S (Defo 1000)	100	100	100
ZnO	5	5	5
S	2	2	3
Vulkacit AZ	1·5	1·5	1·5
PBN	1·5	1·5	1
Paraffin	1·5	1·5	1
Black CK3	20	10	10
Lamp black	25	70	80
Plastikator 88	30	10	—
Naftolen ZD	10	5	—
Cure 30 minutes at 150° C. in each case.			
S.G.	1·16	1·22	1·25
Shore hardness	56	70	86
T_B, kg per sq. cm.	100	107	145
E_B, %	400	310	180
Schopper elasticity, %	54	51	51

Plastikator 88 is the butyl ester of methylene dithioglycolic acid.

TABLE 134. RUBBER SOLES

Buna-S	10
Reclaim	47·5
ZnO	5
PBN	0·5
Coumarone resin	2
Vulkacit DU	1
Sulphur	0·8
Carbon black	24·2
Montan wax	7

Cured 12 minutes at 60 lbs. per square inch.

TABLE 135. SPONGE

Buna-S (Defo 300)	100
ZnO	5
S	2·5
Vulkacit DM	1·2
Dibutylamine	0·25
Naftolen ZD	16
Barytes	40
Brown factice	10
Porofor N	2

Gives 500 per cent. volume increase.

TABLE 136. WRAPPED HOSE COVER AND LINING

Buna-S (Defo 250)	50
Reclaim (Buna tread)	50
Black CK4	15
Black P.1250	12·5
ZnO	2·5
Sulphur	1·25
Vulkacit AZ	1·15

Reclaiming of Buna Rubbers. Where fabric was present in Buna products as in tyres, the conventional alkali treatment was necessary to remove the cellulose. But where no fabric was present one favoured method was a heat treatment together with coumarone resin followed by milling.

Thus 1000 parts of tyre tread were heated in an autoclave with 250 parts of coumarone resin. There was a 2-hour rise to 150 lb. per square inch of steam followed by 6 hours at this pressure and then 8 hours cooling. The mass was then milled until uniform and thereafter sheeted.

Peptizing agents were also used in reclaiming. Particularly effective were the types known as *Renacit.* These included β-thionaphthol,

trichlorothionaphthol, and 9-anthranylmercaptan. The latter was much less toxic than the others. These materials have a variety of applications, being used for heat softening and mastication of the Buna rubbers, as well as for reclaiming.

A typical procedure was to mill into the stock 2 per cent. of Renacit and 10–15 per cent. of plasticizer and then heat in an autoclave at 60 lb. per square inch at 150°–160° C. for 1 hour. Over-treatment caused hardening due to cyclization.

REFERENCES

[1] HAGEN, *Kautschuk*, 1938, **14**, 203.
[2] ROELIG, *Elecktrotech.*, 2, 1938, **59**, 172.
[3] SMITH, AMBELANG and GOTTSCHALK, *Ind. Eng. Chem.*, 1946, **38**, 1167.
[4] STÖCKLIN, *Kautschuk*, 1939, **15**, 1.
[5] C.I.O.S., XXVIII–13.
[6] C.I.O.S., XXXI–75.
[7] C.I.O.S., XXX-103.

TABLE 137. ADVANTAGES AND DISADVANTAGES OF EITHER NATURAL

Field of application	Buna type	Advantages compared with natural rubber
Tyres, inclusive of inner tubes, curing bags and repair material Solid tyres	Buna-S3	Not so sensitive towards overcure Better abrasion resistance
Cycle tyres	Buna-S3	See Automobile tyres
Technical rubber goods		
1 Conveyor belts, transmission belts, V-belts	Buna-S3 Perbunan resp	Better heat resistance for carrying hot materials Not so sensitive towards overcure Better ageing properties
2 High pressure (rubber-asbestos) gasket material	Buna-S3	Better heat resistance
3 Rolls		
(*a*) Textile and paper rolls	Buna-S3	Not so sensitive towards overcure, uniform hardness, higher resistance towards thermal and chemical requirements
(*b*) Printing rolls	Perbunan	Better wear in practical service, oil resistant
4 Rubber lining for chemical purposes	Buna-S3, Buna-85	Higher chemical and heat resistance
5 Packings and sealings	Buna-S3 Perbunan	Higher resistance towards chemical and thermal influences, better ageing properties
6 Rubber-proofings	Buna-S3	Better ageing properties also in acid cured articles Not sensitive to rubber poisons and overcure
7 Moulded goods	Buna-S3 Perbunan	Ageing and heat resistant oil resistant for special applications
8. Hose with inserts	Buna-S3 Perbunan	Ageing and heat resistant not sensitive to overcure Superiority of Perbunan hose in contact with swelling agents
9 Tubing, profiling	Buna S3 Perbunan	No deformation during cure resistant to ageing and chemical influences
10 Dipped goods	Buna-SS Perbunan Buna-85 resp	Better ageing and sterilizing properties swelling resistance of Perbunan qualities
11 Footwear	Buna-S3, Buna SS	No deformation during cure not sensitive to overcure ageing resistant
12 Soles and heels	Buna-S3	Higher abrasion resistance
13 Rubber threads	Buna-SS	Better ageing properties Fast to boiling and ironing
14 Surgical goods and drug sundries Sheeting (hospital, etc) Built-up articles from sheeting	Buna-S3, Buna-SS partially Perbunan	Better ageing and sterilizing properties, no deformation in steam and hot air cure
15 Sponge rubber	Buna-S3 Buna-SS, Perbunan	Superior ageing resistance No deformation during cure Smaller breakdown capability of being cured in hot air
16 Uncured tape	Buna-S3	None
17 Adhesives	Buna-S3 Buna-SS	None
18 Foodstuff qualities (jar rings, bottle disks)	Buna-SS Buna-S3	Higher resistance towards ageing and sterilization longer life in practical service, no deformation during cure
19 Cables		
(*a*) Wire insulation	Buna-S3 Buna-SS	Better ageing and heat resistance No deformation during cure Capability of being cured in hot air Resistant to rubber poisons
(*b*) Cable sheathing	Buna-S3, Buna-SS, Perbunan	No deformation during cure, better ageing, swelling resistance to solvents and lubricants
20 Moulded ebonite goods	Buna-S3, Buna-SS	None

Rubber or Buna Rubbers in the Different Fields of Application

Disadvantages compared with natural rubber	Which rubber (Buna or natural rubber) is to be preferred	
Inferior handling properties, lack of tackiness and weldability properties. Low physical properties (higher hysteresis). More complicated repair conditions	Carcass and cushion	Natural rubber
	Tread	Buna-S3
	Solid tyres	Buna-S3
See Automobile tyres	Cycle tyres	Natural rubber
Similar difficulties as in the production of pneumatic tyres, but not to the same extent	Conveyor belts	Natural rubber or Buna-S or Perbunan
	Transmission belts	Natural rubber
	V-belts	Perbunan
More unfavourable manufacturing conditions		Natural rubber
More difficult manufacturing conditions		Blends of natural rubber with with Buna-S3
More unfavourable manufacturing conditions, necessity of application of aromatic solvents		Perbunan
None		Buna-S3, Buna-85 and blends with Polyvinylchloride (Igelit PCU) according to the requirement
Generally none, partially more difficult building up properties, not as resistant to static loads as natural rubber		Buna-S3, Perbunan
Discolouring of light colours		Buna-S3, blends with natural rubber
Higher damping losses in antivibration articles		Buna-S3, Perbunan, natural rubber, depending on requirement
More difficult building up properties		Buna-S3, Perbunan, natural rubber, depending on requirement
Inferior physical properties		Buna-S3, natural rubber, depending on requirement
Inferior physical properties discolouring in light, when normally stabilized		Natural rubber, Buna-SS, Perbunan extra
Inferior processing properties		Buna-S3, Buna-SS
None		Buna-S3
Lower physical properties, especially in light qualities, discolouring of the fabric		Natural rubber
Inferior processing properties, lower physical properties, discolouring in light		Natural rubber, Buna-S3 and Buna-SS resp. according to articles
None		Buna-S3, Buna-SS
Inferior in tackiness and stability		Natural rubber
Inferior in adhesive power		Natural rubber
Lower in physical properties, discoloration		Buna-S3, Buna-SS resp.
Inferior in seaming properties, somewhat inferior in electrical properties		Buna-S3, Buna-SS, for special cables natural rubber
None		Buna-S3, Buna-SS, Perbunan
Inferior in processing properties, worse weldability, higher brittleness		Natural rubber

CHAPTER 16

ELASTOMERS—BUTADIENE-ACRYLIC NITRILE COPOLYMERS

Production of Butadiene-Acrylic Nitrile Copolymers. Synthetic rubbers based on copolymers of butadiene and acrylic nitrile have attained great importance for specialized applications. The production is relatively small compared with the GR-S and Buna-S types. Thus production in the U.S. in 1947 was a mere 6,624 tons. German production reached a peak of 4,556 tons in 1943. In contrast, however, they give products having solvent resistance which cannot be attained with GR-S nor with natural rubber. Consequently their continued existence is independent of natural rubber supplies.

The methods of production employed both in the U.S. and in Germany are along similar lines to those used for GR-S and Buna-S. The plant is the same and the processing follows the same pattern. The formulae and conditions used at the Leverkeusen plant are as follows :

TABLE 138. FORMULAE AND OTHER DATA FOR PERBUNAN RUBBERS PRODUCED AT LEVERKUSEN

	Buna-N Perbunan	Buna-NN Perbunan-Extra	Igetex-NN Latex
Butadiene	74	60	60 or 55
Acrylonitrile	26	40	40 or 35
Water	150	200	57
Potassium persulphate	0·20	0·20	0·50 or 0·5
Diproxid (di-isopropyl xanthogen disulphide)	0·30	0·27	0·27
Nekal	3·60	3·60	—
Mepasin	—	—	3·75
$Na_4P_2O_7$	0·30	0·30	0·30
NaOH	0·05–0·10	0·10	0·10
Antioxidant	3·0% PBNA	3·0% PBNA	1% Hydroquinone 2% Oxycresyl-camphane
Reaction temperature C.	30	24	25
Reaction time—hours	25–30	60	30
Type of reaction	Continuous	Batch	Batch
Conversion, — %	75	75	62–65
Nitrile in polymer, — %	26	36	—

The Properties of Perbunan and Perbunan-Extra. Perbunan is a copolymer of butadiene and acrylic acid nitrile. It has a nitrogen content of 7 per cent., corresponding to about 25 per cent. acrylic

nitrile. According to Moll, Howlett, and Buckley[12] the Perbunan being made by the Standard Oil Company of New Jersey consists of 74 per cent. butadiene and 26 parts acrylic nitrile. An increase in the proportion of acrylic nitrile was found to enhance the resistance to oils and solvents. Simultaneously, however, the synthetic rubber became more thermoplastic with an accompanying decrease in rubbery properties. The best balance is obtained when the acrylic nitrile content is about 35 per cent. This modified product is Perbunan-Extra. In discussing these rubbers the term Perbunan is used except where other specific proprietary types are considered.

There are a number of proprietary materials which vary slightly in composition and properties.

	Acrylic Nitrile	Butadiene
Chemigum 1 contains 7·1 per cent. nitrogen		
Stanco Perbunan contains 8 per cent. nitrogen	25	75
Hycar O.R.-15 contains 10·5 11·5 per cent. nitrogen	45	55
Hycar O.R.-25	35	65
Butaprene		
Thiokol RD		

All these materials generally contain a stabilizer, usually of the antioxidant class such as phenyl-β-naphthylamine.

They are pale, rubbery materials without marked odour or taste. They are particularly distinguished by their outstanding resistance to swelling by petrol, lubricating oil, and many organic solvents. Apart from this, vulcanized products have other superior physical properties. Both types are better than natural rubber in withstanding heat, in their resistance to abrasion, and in their ageing characteristics. The raw materials are insoluble in aliphatic hydrocarbons, but are freely soluble in aromatic hydrocarbons and chlorinated solvents, they also dissolve in ketones such as acetone.

Processing follows the pattern used for natural rubber. Sulphur is necessary for vulcanization, the rate being speeded up by accelerators. Zinc oxide and stearic acid are used as activating agents. Less sulphur is required than for rubber, 2 per cent. being the usual amount employed.

Both the favourable and unfavourable properties of Perbunan are attributed to its internal structure. Whereas rubber is thought to consist of open long-chain molecules based on isoprene, Perbunan is considered to have a cyclized molecule. Although composed of a large number of butadiene and acrylic nitrile units, it is thought that a mass of long-chain molecules have been formed to yield a cyclized structure. This would provide a plausible explanation for the differences of plasticizing and also its resistance to solvents.

The Perbunans are best handled on two roll mills such as are widely used for rubber processing. As a preliminary, they must be broken down just in the same way as rubber is masticated. The object is to render the material thermoplastic, so that fillers and other ingredients may be added. The breaking down of Perbunan is much more difficult than with rubber. This is one of the chief drawbacks of the material. Breakdown is accomplished by passing through tight cooled mixing rolls. The tighter the rolls the more rapid the breakdown. It is important that the heat developed during this milling should be effectively dissipated, which implies satisfactory cooling. This breakdown or premastication is of fundamental importance and must be adequately carried out. After it the material is soft and stringy. This material is then ready for further compounding. Once premasticated it can be stored and used as required, needing only to be warmed up on the mill for processing. Further breakdown will not be necessary.

At one time it could not be worked in internal mixers, such as the Banbury, which is the backbone of large-scale production. This has recently been overcome. Thus Moll, Howlett and Buckley found that Perbunan can be mixed in the Banbury at the high temperature of 105° C. in the presence of 0·9 part xylyl mercaptan. The time required is between 5 and 20 minutes.

Only small batches of Perbunan can be handled at a time. For example, only 50 lbs. can be used on a 60-inch mill and 120 lb. on an 80-inch mill. The rolls have to be kept cool and very close together, when the initial breakdown then takes about a half-hour. This initial " nerve " of Perbunan is never eliminated by overmastication; it cannot be " killed " in the same way as rubber.

During the breakdown it is sensitive to temperature. Because it is so much tougher than rubber considerable heat is developed on the mill. But at high temperature the material tends to become " short ". It begins to break away from the front roll and becomes unmanageable. It will not take up fillers in a satisfactory manner, forming large indispersed pockets of material.

The heat-softening procedure developed for Buna-S does not work with these other derivatives. However, other chemical methods are being developed with some success. The chemical peptizers which are found to be so effective for GR-S and Buna-S are equally effective with nitrile rubbers.

Compounding Perbunan. The normal range of compounding ingredients are incorporated, e.g. sulphur, accelerators, zinc oxide, fillers, etc. There is one important addition, more fundamental

than in the case of rubber, namely, plasticizers. Compounding may be carried out in the Banbury mixer. It is usual to adopt devices such as additions of rubber or reclaim or ready-mixed Perbunan stock to facilitate the mixing. Plasticizers and softeners are added to aid the process. Perbunan works very dryly and lacks tackiness, consequently the softeners normally used with rubber are not adequate.

In the ordinary way premasticated material is put on to the mill and allowed to form a band. Then zinc oxide and accelerators are incorporated, being well blended into the material. Plasticizers come next, followed by the fillers, and finally sulphur. Great care is necessary to ensure adequate dispersion. The best practice is to finish the mixing off, allow it to cool and then refine it by passing through very tight rolls. This ensures effective dispersion.

The Use of Plasticizers. Perbunan is much less thermoplastic than natural rubber. A suitable selection of plasticizers greatly facilitates the improvement of plasticity and also aids such other properties as tackiness, the extrusion process, etc. Another important point is that most available plasticizers also lower the cost of the compound. In the normal way the addition of softeners would be of the order of 5–10 per cent. of the amount of Perbunan. For exceptional purposes the plasticizer content may be as high as 150 per cent.

Four types of plasticizers may be used with Perbunan. The general range of plasticizers employed in plastics technique and lacquer technique such as dibenzyl ether, triphenyl phosphate, phthalic acid esters, dibutyl sebacate, etc., are very effective. They all have a marked softening effect on the material, but nevertheless profoundly improve the elasticity of the vulcanized composition. These plasticizers swell the Perbunan, but do not affect the processing properties to any great extent.

It is essential to add additional softeners to enhance the tackiness of the unvulcanized material. As a matter of fact this is a very important feature of nearly all synthetic elastics. They greatly affect such processes as lamination and the building of all plied material as in the manufacture of beltings or hose. In most cases these softeners reduce the elasticity of the vulcanized material. Amongst the chief materials that are used are rosin, coumarone resin, rosin oil, alkyd resins, coal tar, pine tar, etc. It will be recognized that these materials perform a precisely similar function with natural rubber compounds.

Perbunan compounds do not extrude and calender so well as natural rubber owing to the fact that they have considerable nerve and are lacking in plasticity. Consequently suitable materials must be added

to facilitate extrusion and calendering. Typical materials which help these features include alkyd resins, lanolin, and factices.

There is one other type of softening material which should be considered in connection with Perbunan. The outstanding property of Perbunan is the resistance to oils and solvents. In order to attain a maximum resistance to these solvents, it is obviously essential that materials used as plasticizers should, as far as possible, be insoluble in petrol and oil. Examples of such softeners are triphenyl phosphate, alkyd resins, trichlorethyl phosphates, etc.

In this connection Stöcklin [16] showed that addition of another class of synthetic rubber-like material profoundly enhanced the oil-resisting properties of Perbunan. He found that addition of polysulphide condensation rubbers of the thioplast type greatly improved the already excellent oil-resisting properties of Perbunan. These materials were mixed in on the rolls. The products were found to have remarkable swelling resistance and other physical properties. It should be noted that this procedure of adding thioplast to other synthetic rubbers has proved very successful. For example, similar materials are added to neoprene and also to one type of Thiokol—Thiokol RD—which contains butadiene.

Thus a typical mix employed for Perbunan to be used in contact with petrol, comprises Perbunan 75, Thiokol F 25, Dibutyl phthalate 5, plus the usual accelerators, etc.

Strangely enough, one of the best softeners for Perbunan is natural rubber. It is found that additions of up to 20 per cent. do not greatly detract from the swelling characteristics while facilitating the processing. The primary effect of using any great amount of rubber together with Perbunan is to lower the resulting oil resistance and to detract seriously from the ageing characteristics and ability to withstand high temperature service.

However, in many applications low proportions of rubber can be used with great benefit in all the processing aspects. Reclaim, too, may be substituted, conferring advantages in processing and increasing the tackiness. As would be anticipated, oil resistance is lowered and so is the tensile strength.

Other plasticizers recommended include tributyl phosphate, dibenzyl sebacate, butyl acetyl ricinoleate, etc.

Plasticizers employed for synthetic elastic materials in many cases differ from those normally employed for rubber technology. Among the most extensively used are materials such as tricresyl phosphate, dibutyl phthalate, dibutyl sebacate, etc. These are widely used in the manufacture of lacquers, varnishes, coatings, etc., and in the plastics industry.

The properties which are sought in plasticizers, apart from the ability to mix, include:

(*a*) Non-volatility and non-inflammability.
(*b*) Good retention by the material, i.e. there must be no sweating.
(*c*) Good water resistance.
(*d*) Resistance to petrol and oils.
(*e*) Low freezing point.
(*f*) Odourless, chemical stability, non-toxicity, etc.
(*g*) Good electrical properties.

Very few come up to all these requirements, and plasticizing is invariably a compromise.

Tricresyl phosphate is a colourless, odourless liquid, with a specific gravity of 1·175. It has a high boiling point of 295° C. at 13 mm. pressure. It freezes at - 35° C. It has a very low water solubility—less than 0·002 per cent. at 100° C. It is probably the most widely used plasticizer. It has a high temperature stability, and is unaffected by acids and alkalis. It has good fire-retarding properties.

Another very widely used plasticizer is dibutyl phthalate, which is a clear, colourless liquid, boiling at 340° C. and freezing at – 35° C. The specific gravity is 1·048 at 20° C. It is miscible with most organic solvents and oils, but has an extremely low water solubility amounting to 0·001 per cent. at 20° C.

Another less-well-known plasticizer, which is, however, attaining great importance particularly for elastomers, is dibutyl sebacate, which has a specific gravity of 0·940 at 25° C., and a boiling point of 340° C. This also has a very low solubility in water—less than 0·1 per cent.

Addition of Filling Materials to Perbunan. Filling materials are always added to Perbunan, not only because they are necessary to cheapen the product but because the unloaded Perbunans yield vulcanized products which are much weaker than the corresponding rubber articles and have very limited scope. The usual range of rubber fillers are widely used, including zinc oxide, china clay, whiting, lithopone, etc.

As with rubber, the best properties are brought out by the use of strong reinforcing fillers. From this point of view and from the point of view of cost, Perbunan is usually compounded according to the requirements. All classes of hard carbon blacks produce products with high tensile strength and good abrasion resistance. They enable the production of materials having tensile strength quite as high as the best obtainable with natural rubber, e.g. about 5,000 lbs. per square inch. They also yield Perbunan compounds having the optimum values for

hardness and resistance to tear. However, they do not give the best values with regard to permanent set, the ability to bond to metal and the rebound elasticity.

It is found that addition of semi-reinforcing softer blacks, while giving somewhat lower tensile strength and hardness, yet give a better balance of physical properties and result in the best all-round products. They produce compounds having better flexibility, a maximum of rebound elasticity, less permanent set, better bonding to metals, and the resistance to fatigue and flexing is also augmented.

With the exception of magnesia and magnesium carbonate, which tend to cause hardening up of Perbunan stocks, almost every white filler can be used as in the case of rubber. In some cases some of these

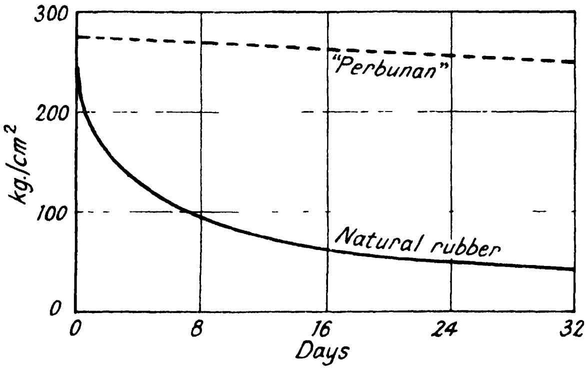


FIG. 76.—Tensile Strength of Perbunan and Rubber Tyre Tread Compounds during Ageing in an Oxygen Bomb at 60° C.[16]

fillers do not give the same tensile strength as they do in rubber. Nevertheless they are very useful in compounding Perbunan for special purposes.

Zinc oxide plays a similar rôle to that which it plays in rubber compounds, and is primarily useful in small amounts to activate the accelerators. Usually from 2 to 5 per cent. is adequate for this purpose. It is found that larger quantities of the order of 15 parts are helpful with mercaptobenzthiazole as an accelerator in order to achieve a strong bond to metal. As in rubber, zinc oxide helps to maintain the tackiness of compounds, which are to be plied together as in belt and hose friction materials. Since zinc oxide is not easily wetted and dispersed by Perbunan, it is desirable to add it early in the compounding process to ensure thorough dispersion.

Other white fillers such as clay, whiting, blanc fixe, and barytes are primarily useful in Perbunan only as cheapeners, and as might be

expected, this is achieved at the expense of the tensile strength, elasticity, and permanent set. These inert fillers perform a very useful function by aiding processing, and their presence materially improves the extrusion and calendering properties of Perbunan.

This type of elastomer as manufactured contains about 2 per cent. of antioxidant phenyl-β-naphthylamine, a quantity which is adequate to protect it for all normal applications. It darkens on exposure to light, and consequently limits the use of Perbunan for light-coloured articles. As in the case of rubber, the best heat-resisting compounds are made with thiuram accelerators, and for such applications it is desirable to add a small further amount of antioxidant.

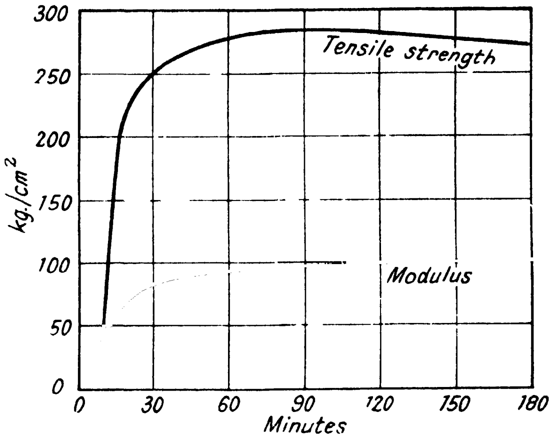


FIG. 77.—Tensile Strength and Modulus of a Perbunan–Carbon Black Mix during Progressive Vulcanization.[16]

It is essential to add waxes in Perbunan compounds which are to be made into mechanical goods or any product which may have to stand up to sunlight or be subject to flexing. In this respect Perbunan appears to be just as vulnerable as rubber. The most suitable waxes include paraffin wax, ozokerite, ceresine, petroleum waxes, etc. In addition to the protection thereby afforded, they also assist the processing of the compounds.

As in the case of rubber, stearic acid is used with Perbunan to assist in the dispersion of carbon black, and to act as an activator for various accelerators. Up to 3 per cent. may be employed to advantage. It does not mix into Perbunan very easily, and is generally added together with fillers. Stearates may be added to Perbunan in very much the same manner as to rubber.

Vulcanization Characteristics. The vulcanizing behaviour of

Perbunan is very similar to that of rubber; rather less sulphur is necessary for soft products, about 2 per cent. being generally used. The temperature coefficient is of the order 1·5 for 10° F. Selenium and tellurium are also effective.

The normal vulcanizing temperatures employed with Perbunan compositions is between 125° and 150° C., while the time of vulcanization in general varies from 10 to 60 minutes. Continued heating of Perbunan vulcanizates is accompanied only by slight hardening and can be regarded as a form of after-vulcanization; there is no tendency for tackiness or resinification to occur as in the case with rubber.

The table illustrates the effect on various properties of variations in the sulphur content of a specimen Perbunan compound. The lower sulphur requirement may be due to the fact that Perbunan has less unsaturation than rubber.

TABLE 139. INFLUENCE OF SULPHUR ON PERBUNAN [11]

Perbunan	100
Dibutyl phthalate	10
Coal tar	5
Rosin	5
Stearic acid	2
Zinc oxide	5
Spheron	30
Altax	1·25
Dibutylamine	0·25
Sulphur	as in the table following

Press cure 40 minutes at 141° C.

Sulphur	T_B lbs./in.^{2}	E_B %	M300	H
1	3180	750	420	50
2	3400	650	560	55
3	2820	500	1000	58
5	1970	300	1970	61
7·5	1820	200	—	65
10	1660	175	—	70

From this table it is easy to see that in this particular compound, which is typical, a sulphur content over 2 per cent. produces two principal effects. First, the higher ranges of sulphur produce rapidly increasing hardness and modulus, while the elongation correspondingly decreases. Optimum tensile strength is attained with a sulphur content not greater than 2 per cent.

The use of accelerators in the vulcanization parallels the ordinary rubber practice. The most useful types include mercaptobenzthiazole, benzthiazyl disulphide, particularly when used together with diphenylguanidine or di-orthotolyl guanidine. The organic ultra-accelerators

function precisely as with rubber. As with rubber the dangers of premature vulcanization during processing must be considered.

As in the case of rubber, added resistance to heat is obtained by using ultra-accelerators which carry their own sulphur of vulcanization, notably the thiurum disulphides. Sulphur as such is omitted. Such heat-resistant products are much superior to their rubber prototypes. They show no tendency to tackiness, nor does the phenomenon of reversion occur. Prolonged exposure to heat merely causes slight hardening up. The use of ultra-accelerators enables the production of materials which will vulcanize at low temperatures, even at room temperature. High sulphur content and high accelerator content appear to be necessary. Thus with 4 parts sulphur and 3 parts zinc isopropyl xanthate, vulcanization at 20° C. takes 4 days.

Ageing of Perbunan. These Perbunan materials have excellent resistance to ageing. They are superior to corresponding rubber compounds. While addition of antioxidant is not really necessary owing to the amount already present, further antioxidant can enhance the ageing behaviour. It is affected by sunlight or ultra-violet light. When carbon black is present the effect is minimized.

TABLE 140. AGEING OF PERBUNAN

		Parts by weight
Perbunan		100·0
Zinc oxide		5·0
Stearic acid		1·0
Trimethyl dihydroquinoline type antioxidant *		2·0
Protective Wax †		2·5
Fine thermal black		50·0
2-cyclohexaminobenzothiazyl sulphide ‡		3·0
Tetra methyl thiuram disulphide		3·0
Original physical properties cure, 30 minutes at 287° F.:		
Tensile, p.s.i.		2510
Elongation at break, per cent.		830
Modulus at 300 per cent.		300
Shore Durometer hardness		42
Oven Ageing at 300° F.	45 hours	70 hours
Tensile, p.s.i.	1510	1130
Elongation at break per cent.	310	195
Shore Durometer increase	13	18
180° sharp bend test	no cracking	no cracking

* Santoflex B; Agerite Resin D.
† Sunproof; Heliozone; Antisol.
‡ Santocure.

Hard Rubbers Based on Buna Elastomers. With more than 30 per cent. of sulphur, hard materials result which in some respects are superior to ebonite, notably in resistance to solvents and in greater heat resistance.

A very informative study on hard rubbers obtained from Buna elastomers has been made by Gartner.[6] He prepared comparable mixes based on the elastomers and subjected them to electrical tests.

TABLE 141. COMPOSITIONS OF THE HARD RUBBER MIXTURES [6]

No	Natural rubber		Buna-85		Buna-S		Buna-SS		Perbunan		Perbunan-Extra	
	1	2	3	4	5	6	7	8	9	10	11	12
Rubber (percentage by weight)	75·0	73·3	73·3	71·7	77·8	76·0	79·1	77·3	79·7	78·5	79·7	78·5
Sulphur (percentage on rubber)	32·0	35·0	35·0	38·0	27·0	30·0	25·0	28·0	24·0	26·0	24·0	26·0
Natural rubber	100·0	100·0	—	—	—	—	—	—	—	—	—	—
Buna-85	—	—	100·0	100·0	—	—	—		—	—	—	—
Buna-S (Defo 250)	—	—	—	—	100·0	100·0	—	—	—	—	—	—
Buna-SS (Defo 400) . .	—	—	—	—	—	—	100·0	100·0	—	—	—	—
Perbunan	—	—	—	—	—	—	—	—	100·0	100·0	—	—
Perbunan-Extra	—	—	—	—	—	—		—	—	—	100·0	100·0
Sulphur	32·0	35·0	35·0	38·0	27·0	30·0	25·0	28·0	24·0	26·0	24·0	26·0
Vulkacit DM	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5
Totals	133·5	136·5	136·5	139·5	138·5	131·5	126·5	129·5	125·5	127·5	125·5	127·5

He found that Buna-S hard rubbers were almost as good as those made from natural rubber, while those made with Buna-SS were superior. As might be expected, those made with Perbunan were not so good, but were better than expected.

TABLE 142. ELECTRICAL PROPERTIES OF HARD RUBBERS (1000 V.) [14]

Rubber	Sulphur	Ohms per cm $\times 10^{16}$		tan δ (50 Hertz)		Dielectric constant (50 Hertz)	
	%	(1)	(2)	(1)	(2)	(1)	(2)
1. Natural rubber	32	8·4	Higher than 10^{16}	0·0056	0·0050	2·9	2·9
2. Natural rubber	35	8·8	Higher than 10^{16}	0·0056	0·0066	2·9	2·9
3. Buna-85 . . .	35	10·0	Higher than 10^{16}	0·0076	0·0067	2·9	2·9
4. Buna-85 .	38	10·0	Higher than 10^{16}	0·0077	0·0078	3·0	3·0
5. Buna-S . . .	27	6·8	Higher than 10^{16}	0·0057	0·0050	3·0	3·0
6. Buna-S . . .	30	4·7	Higher than 10^{16}	0·0047	0·0051	2·9	2·9
7. Buna-SS . .	25	10·0	Higher than 10^{16}	0·0029	0·0035	2·9	2·9
8. Buna-SS . .	28	10·0	Higher than 10^{16}	0·0033	0·0045	3·0	3·0
9. Perbunan . .	24	2·6	Higher than 10^{16}	0·0014	0·0084	4·0	4·0
10. Perbunan .	26	5·4	Higher than 10^{16}	0·0096	0·0088	3·9	3·9
11. Perbunan-Extra .	24	5·0	Higher than 10^{16}	0·0098	0·0101	4·2	4·2
12. Perbunan-Extra .	26	3·2	Higher than 10^{16}	0·0093	0·0114	4·1	4·2

(1) Original state.
(2) After 14 days in air oven at 100° C.
The compositions are given in Table 141.

Hard rubbers are widely employed on account of their resistance to corrosion. So Gartner also studied the behaviour of the various elastomer hard rubbers on contact with the more usually encountered chemical agents over long periods of time. Table 143 summarizes the results obtained.

The elastomer hard rubbers displayed exceptionally good resistance to even the most exacting corrosive agents.

According to Bruce, Lyle and Blake [3] the heat of vulcanization of Perbunan indicates the presence of two chemical reactions. Unlike natural rubber and GR-S, the ebonite reaction does not predominate until sulphur concentration is raised above 10 per cent.

TABLE 143. CHEMICAL STABILITY OF THE HARD RUBBERS

Reagent	Very satisfactory	Unsatisfactory
Water (8 weeks at 95° C.)	Buna-85, Buna-S and Buna-SS vulcanized in steam Natural rubber	
Hydrochloric acid (12 weeks at 20° C.)	Natural rubber Buna-85 Buna-S Buna-SS Natural rubber (All equally good)	Perbunan Perbunan-extra
Sulphuric acid (Dilute) (12 weeks at 20° C.)	Natural rubber Buna-85 Buna-S Buna-SS (All equally good)	Perbunan Perbunan-extra
Hydrofluoric acid (2 weeks at 20° C.)	Heavily loaded blends of natural rubber with Buna-85 Neoprene Buna-SS	Perbunan Perbunan-extra
Nitric acid (8 weeks in 32% at 20° C.)	Buna-SS (Both vulcanized in hot air)	Perbunan Perbunan-extra
Chlorine gas (4 weeks at 70° C.)	Buna-85 vulcanized in steam Natural rubber	Perbunan Perbunan-extra (Both vulcanized in steam)
Sodium Hypochlorite (8 weeks at 20° C.)	Buna-85 Buna-S Buna-SS Perbunan Perbunan-Extra. (In all cases, particularly when containing high percentages of sulphur and vulcanized in hot air)	
Benzene (8 weeks at 20° C.)	Perbunan-Extra (with high proportions of sulphur)	Natural rubber Buna-85 Buna-S Buna-SS

Processing of Perbunan Compounds. All the usual processing methods applied to natural rubber may be used with equal success in handling Perbunan compounds. The precautions to be taken for various fabrication processes are much the same as with natural rubber. As is the case with every material there are certain knacks which can only be acquired by experience.

Press-curing of Perbunan presents no difficulties as the material flows extremely well. The plateau effect in the curing of Perbunan renders the time of cure less critical than with natural rubber, since overcure does not greatly lower the physical properties.

Open steam-curing of Perbunan compounds works perfectly well, generally yielding vulcanized stocks rather harder than if the same stock is press-cured.

TABLE 144. PROPERTIES OF COMPARABLE VULCANIZED PRODUCTS

Basis	T_B kg./cm.	E_B %	M_{300}	H	Pendulum elasticity
Raw rubber	260	600	70	65	50
Perbunan	300	600	90	70	45
Buna-S	275	650	80	65	50

Calendering or frictioning of Perbunan compounds presents no difficulty if they are designed for the purpose. In general, any normally plasticized Perbunan compound may be calendered into thin sheets without trouble if the roll temperatures are suitably adjusted.

Fairly highly filled Perbunan presents few difficulties for preparing calendered sheet. Roll temperatures are normally between 110° F. and 160° F.

Frictioning compounds must contain high proportions of tack-producing softeners.

In frictioning compounds they generally tend to stick to the cooler roll in contrast to rubber stocks. Usual conditions are middle roll temperatures between 125° and 180° F. with top roll temperatures 10° F. higher. The bottom roll is kept hot at about 200° F.

Mixtures of pine tar and dibutyl phthalate are useful for frictioning, while addition of reclaim improves the tackiness.

Tubing or extruding of Perbunan proceeds very easily when the compound is plasticized with those softeners particularly recommended for this purpose. Lubricating agents such as stearic acid, degras, paraffin wax, etc., are advantageous for extrusion in amounts up to 3 per cent. In general the barrel and worm of the extruder should be

thoroughly cold, and the head may be warmed up to 200° F. The die should be only sufficiently warm to assure that the stock extrudes smoothly. Roughness may be attributable to unsatisfactory mixing.

Bonding Metal and Perbunan. The bonding of Perbunan to metal is comparatively simple to achieve in the case of iron, steel, and ferrous alloys generally. An intermediate coat of chlorinated rubber is used as a bonding agent. The metal surface should be thoroughly cleaned and free of grease in any case; it should preferably be sand-blasted, pickled or treated with an abrasive paper to produce a slightly roughened surface to improve the bond. Then there should be applied to the properly prepared metal surface two or three coats of a 15 per cent. solution of chlorinated rubber (125 cp. viscosity) dissolved in toluene. The best bond will result if, before vulcanization,

TABLE 145. AGEING OF COMPARABLE MIXES LOADED WITH CARBON BLACK

Basis	Original		Geer oven (90° C) 32 days		Oxygen bomb 32 days	
	T_B	E_B	T_B	E_B	T_B	E_B
Raw rubber	260	600	130	350	50	200
Perbunan	290	560	260	400	250	600
Buna-S	270	765	225	575	230	600

the raw Perbunan compound can be formed so that it will conform fairly well to the metal surface and hence flow as little as possible in the mould. It is preferable to join the coated metal and the preformed Perbunan while the last coat of chlorinated rubber is at least still somewhat moist with solvent and tacky.

From the electrical viewpoint, Perbunan has little to offer. Thus it has a dielectric constant of 15, and a specific resistance of 10^7 ohms/cm.[3] It is virtually a semi-conductor and finds some use as such in the new field of conducting rubbers.

Oil Resistance of Perbunan. The outstanding property of Perbunan is the solvent resistance, particularly as shown by properly compounded vulcanized products. The oil resistance is considered to be due partly to the presence of the —CN group and partly to cross-linking. Although excellent in resistance to petroleum solvents increased resistance to aromatic solvents is desirable. The influence of numerous types of solvents and oils is summarized in the following

table. It is remarkable how the tensile strength is retained after contact with these solvents and oil.

TABLE 146. SWELLING OF UNPLASTICIZED PERBUNAN COMPOUND AFTER 8 WEEKS AT ROOM TEMPERATURE [10]

Original Tensile Strength 2600 *lb./in.*^{2}

	Percentage increase in weight	Tensile strength lb./sq. in. Swelled sample
Petroleum fraction, propane, butane, petrol, mineral oil, etc.	0– 10	2100/2500
Transformer oil	0– 10	2400
Fuel oil	0– 10	2300
Paraffin oil	0– 10	1850
Benzol, toluol, xylol	50–100	700
Carbon tetrachloride	50–100	850
Methylene chloride, chlorbenzene, etc.	more than 100	400/700
Esters, ketones, aldehydes, amines	50–100	400/600
Alcohols	0– 20	1700/1850
Glycols	0– 10	2400/2500
Palm oil, fish oil, butter	0– 20	2100/2500
Linseed oil	10– 20	1950
Oleic acid	20– 50	2500

Quite clearly it is exceptionally resistent to aliphatic hydrocarbons, while being susceptible to aromatic hydrocarbons. It is eminently suited to withstand lubricating oils. It is also outstanding in its resistance to mineral and vegetable oils.

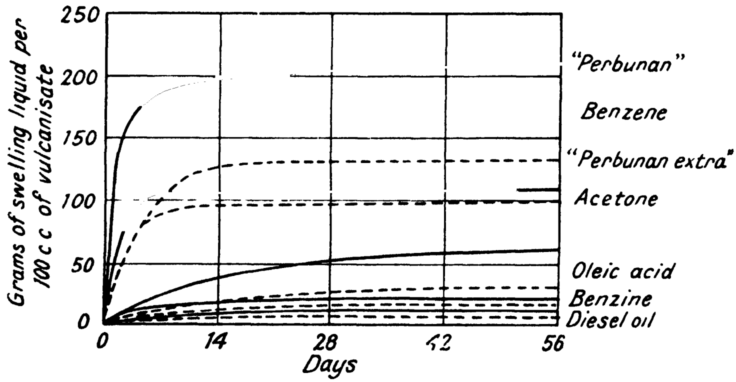


FIG. 78.—Swelling of Perbunan in Various Solvents.[16]

The swelling action of different types of solvents on Perbunan compounds varies widely. It is true that the more highly loaded a Perbunan compound is the less it will swell in a given solvent, although this is much less important than with the natural rubber compounding.

TABLE 147. HOSE COMPOUND WITH HIGH RESISTANCE TO SWELLING [16]

1. *Tube and cover.*		2. *Friction.*	
100·0	Perbunan-Extra	100·0	Perbunan-Extra
8·0	Rosin	50·0	Dibenzyl ether or coal tar fuel oil
3·0	Softener III	15·0	Carbon black
25·0	Dibenzyl ether	30·0	P.33
15·0	Carbon black	5·0	Zinc oxide
120·0	Thermax, P.33 or Gastex	1·3	Sulphur
125·0	Whiting	1·0	Vulkacit AZ
5·0	Zinc oxide		
2·2	Sulphur		
1·5	Vulkacit AZ		

Cure in steam : 40 to 50 min. : 45 lbs. per sq in.

	T_B.	E_B.	M_{300}.	H.	E.
Physical properties of mixing (1)—					
with Thermax	65	360	59	76	28
with Gastex	90	225		85	21
with P.33	78	480	56	77	20
Physical properties of mixing (2) —					
with dibenzyl ether	72	910		30	51
with coal tar fuel oil	84	1050		33	47

	Benzol	Coal tar fuel oil	Petrol	Fuel mixture
Swelling of the tube stock (1) in 24 hours at 70°	45%	90%	0·2%	11%
Test immediately after swelling T_B	31	28	71	60
E_B	140	150	190	180

The fuel mixture consists of 75% petrol, 10% benzol, and 15% alcohol.

There is no great difference between low and high loadings so far as solvent swelling is concerned. For minimum values of solvent swelling or absorption, it seems essential that Perbunan compounds should be fully cured or even slightly overcured.

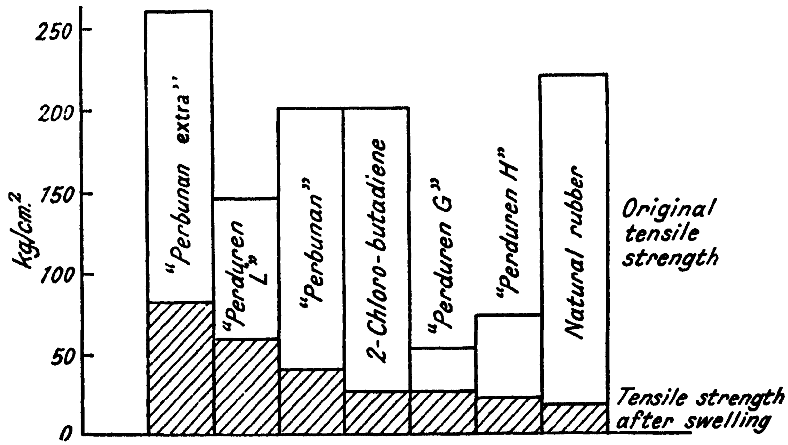


FIG. 79.—Tensile Strength after Swelling for 8 weeks in Turpentine at 20° C.[16]

None of the common alcohols and glycols used for anti-freeze purposes swells Perbunan appreciably. But many applications of Perbunan compounds for service in contact with anti-freeze liquids require good resistance.

Apart from the better solvent resistance and heat-resisting properties of Perbunan compounds, it is claimed that they have far superior resistance to abrasion. A Perbunan tyre tread mix is claimed to be considerably better in this respect than a corresponding tread mix of rubber.

TABLE 148. STANDARD PERBUNAN FORMULAE—MOULDED ARTICLES [20]

Perbunan		100	100	100	100
ZnO		5	6	6	5
S		2	2	2	1·5
Vulkacit AZ		1·5	1·5	1·5	1·5
PBN		1·5	1·5	1·5	—
Paraffin		1	1	1	1
CK3 black		—	25	10	10
Lamp black		50	40	70	100
Plastikator 88		40	30	25	20
Naftolen ZD		15	15	5	—
S.G.		1·15	1·2	1·23	1·28
Shore H.		46	55	70	85
% elasticity		50	40	43	38
T_B, kg./cm.^{2}		67	104	122	146
E_B, %		510	390	300	185
% Swell	Weight/volume				
Motor spirit	24 hours	60/90	55/85	50/80	45/75
	100 ,,	60/90	55/85	50/80	45/75
Lubricating oil	100 ,,	−12/ 25	−20/−20	−12/−12	−10/−10
Coolant	100 ,,	−12/−12	−10/−10	±5/+5	+5/±5
Water	100 ,,	+3/=3	-3/ 3	±3/−3	5/5
Brake fluid	100 ,,	12/−10	−10/−8	5/−3	+2/+3
Spindle oil	100 ,,	−20/−20	−15/−15	−10/−10	−8/−8

Resistance to Heat and Cold. The resistance of Perbunan compounds to low temperature is, in general, similar to that exhibited by natural rubber compounds. When properly compounded Perbunan may be used at temperatures of 300° F. The different behaviour towards heat of butadiene rubbers compared with natural rubber is worth stressing. Natural rubber compounds when subjected to high temperatures usually tend to soften and become tacky—they " revert ". This can be prevented by careful compounding. However, most rubber articles should not be used above 100° C., while even specially designed types cannot be used above 130° C. By contrast, synthetic rubbers when heated harden up and tend to become " short ". Thus while Perbunan, Chemigum, Hycar, etc., and GR-S can be used up

to 150° C., these facts must be considered. Their utility at high temperature will depend largely on the initial hardness and they should clearly be as soft as possible initially. At the other end of the scale, it cracks at − 45° F. It is necessary to incorporate suitable plasticizers, to bring out the best low temperature characteristics, e.g. resistance to hardening and to shattering. The best materials include: tributoxy ethyl phosphate, dibutyl sebacate, dibutyl phthalate, tributyl phosphate, dibenzyl sebacate, butyl acetyl ricinoleate, etc.

TABLE 149. STANDARD PERBUNAN FORMULAE—EXTRUDED ARTICLES [20]

Perbunan		100	100
ZnO		5	5
S		1·8	1·8
Vulkacit AZ		1	1
Vulkacit DM		0·8	0·8
PBN		1·5	1·5
Paraffin		1·5	1·5
P.1250 black		25	20
Lamp black		40	70
Factice		Soft 25	Hard 20
Plastikator 88		30	20
Naftolen ZD		20	10
S.G.		1·17	1·2
Shore H.		45	70
Elasticity		40	37
T_B kg./cm.^{2}		78	114
E_B %		550	270
% Swell	Weight/volume		
Motor spirit	24 hours	55/80	50/80
	100 ,,	55/80	50/80
Lubricating oil	100 ,,	−20/−25	−15/−20
Coolant	100 ,,	−10/−15	−8/−10
Water	100 ,,	5/8	5/8
Brake fluid	100 ,,	−5/−10	−8/−10
Spindle oil	100 ,,	−10/−12	−12/−15

Heat resistance of Perbunan compounds is inherently superior to that of natural rubber products. Perbunan does not develop tackiness, nor does reversion occur when it is exposed to elevated temperatures. The primary effect of prolonged exposure of Perbunan compounds to heat is to cause a gradual increasing surface hardness while the tensile strength is at first increased, then gradually decreased as the elongation and rebound elasticity fall off. At the present time maximum resistance of Perbunan compounds to high temperatures seems to be accomplished along the same lines as with rubber, through the use of tetramethyl-thiuram disulphide, with little or no sulphur. The presence of semi-reinforcing blacks or soft carbon blacks is beneficial.

Uses of Perbunan. Perbunan and Perbunan-Extra are widely employed in the production of:

Gaskets, packings, seals, food containers, motor-car parts, petrol hose, oil-resistant sheetings, etc.

They are attached to metal parts and find great application for use in engineering both in extension and under compression.

TABLE 150. HEAT-RESISTING PERBUNAN COMPOUNDS [17]

Perbunan	100·0	100·0
P.33	30·0	30·0
Thermax	30·0	30·0
Zinc oxide	1·0	1·0
Softener III	3·0	5·0
Vulkacit Thiuram	2·5	2·5
Antioxidant MB	2·5	2·5
Sulphur	0·1	0·07
Crêpe	12·0	—
Dibenzyl ether	—	10·0

	T_B	E_B	M_{250}	E.	H.	T_B	E_B	M_{250}	E.	H.
Cure at 45 lbs. per sq. in.										
30 min.	93	760	30	48	56	99	980	24	55	54
60 ,,	105	740	34	47	57	105	845	28	55	56
Aged in air at 150° C.										
48 hours	117	385	67	45	68	144	385	84	45	72
	123	387	68	46	68	159	437	84	45	72
96 ,,	87	275	78	42	71	102	275	94	42	74
	96	275	85	42	71	78	237	—	42	74
120 ,,	57	156	—	35	74	49	106	—	35	78
	42	100	—	35	75	41	90	—	36	78
Aged in transformer oil at 150° C.										
48 hours	57	331	35	56	46	117	470	45	55	56
	51	320	33	56	46	105	465	42	55	56
96 ,,	36	262	34	55	44	72	331	48	52	58
	35	260	32	54	44	70	330	46	51	58

Spreading and dipping Perbunan compounds are readily prepared from a wide range of unvulcanized stocks. Thus it is possible to spread and dip cements or solutions of such compounds as will give vulcanized goods ranging from very soft, resilient products to the consistency of hard rubber.

The Use of Perbunan for Spreading and Dipping. Perbunan is successfully used in the manufacture of sheetings and dipped goods. Gloves are the chief products made by dipping. Gloves for various

industrial purposes resistant to oils, benzene, weak and highly concentrated acids, are now made from Perbunan, and they are claimed to be far superior to those made of natural rubber; in fact, for some purposes where they are used, natural rubber cannot be employed at all.

All kinds of nipples and teats are also made. It has not yet been possible to achieve the transparency that had become usual in natural rubber goods of this type, but this is not really necessary.

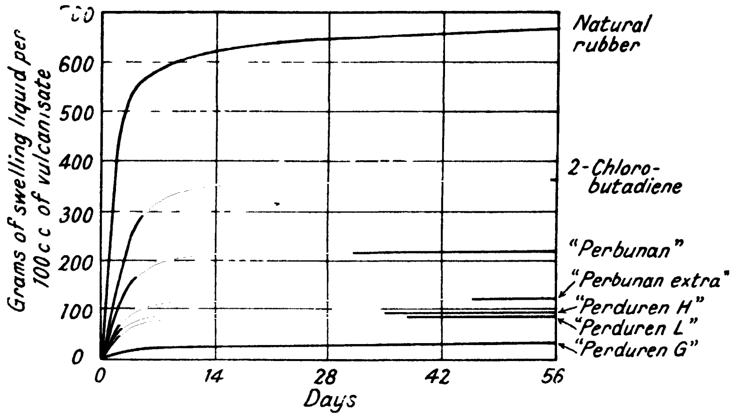


FIG. 80.—Swelling of Perbunan compared with other Elastics in Carbon Tetrachloride at 20° C.[16]

In spite of the outstanding solvent resistance there are a number of solvents which can be used for making solutions for cements or for dipping. These are:

1. Aromatic hydrocarbons such as benzene, toluene, xylene.
2. Powerful petroleum hydrocarbons such as Solvesso No. 1, Solvesso No. 2; Solvesso No. 3.
3. Chlorinated hydrocarbons such as ethylene dichloride.
4. Acetates such as butyl acetate.
5. Ketones such as acetone, methyl ethyl ketone, etc.

Cements may contain up to about 1 lb. solid per gallon of solvent. Spreading doughs contain rather more.

Dipped goods made of Perbunan are, of course, very resistant to oils and solvents.

The manufacturing process, while similar to that followed when natural rubber solutions are used, offers various difficulties which have to be overcome. The Perbunan must be thoroughly broken down. Difficulties are also encountered in preparing solutions. With efficient

mixers it is possible to complete the production of Buna solutions in about four hours. The appropriate solvent for the different types of Buna must be carefully selected. For Perbunan mixes toluene is the preferred solvent.

Another source of trouble is the right concentration and viscosity of Buna solutions. But once the solutions have been properly prepared, the actual dipping process is simpler than with natural rubber solutions. For one thing it is much easier to obtain a Buna solution free of bubbles. One hour after stirring, the latter is usually perfectly free from bubbles, and the dipping process can be interrupted at will to add fresh solution.

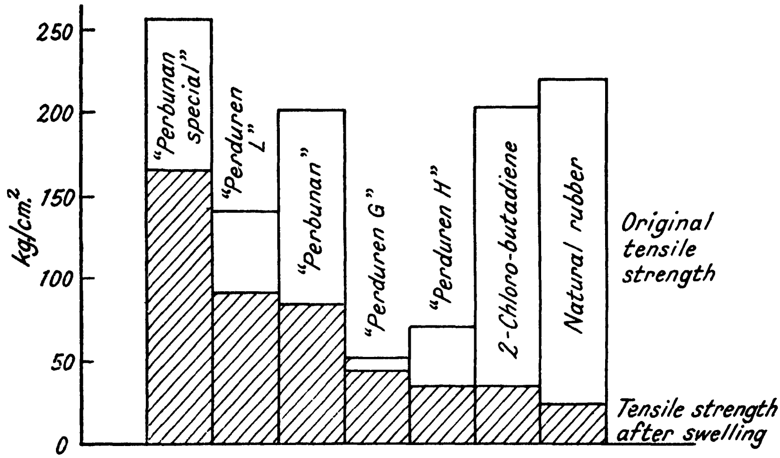


FIG. 81.—Tensile Strength after Swelling for 8 weeks in Carbon Tetrachloride at 20° C.[12]

In addition the dipping and drying operations can be effected more rapidly. However, Buna solutions are generally less concentrated, thus requiring more dippings to obtain the same thickness in the finished goods.

When the goods are finished and have to be rolled, the lower adhesive power of Buna also causes trouble.

No changes have to be introduced in the vulcanization process, generally hot-air curing, which, if anything, is simpler than with natural rubber, because the vulcanization plateau of Perbunan is wider and a slight deviation from the heating limits in either direction is not nearly so unfavourable in its effect on the product.

The cured goods are removed from the moulds in the usual manner, but here again the structure of Perbunan becomes apparent, and removal is more difficult.

Perbunan-Extra. Perbunan-Extra has even better oil- and solvent-resisting properties than the ordinary Perbunan. The larger proportion of acrylic acid nitrile present is thought to lead to a lesser degree of cyclization in the molecule. As a result, it is more easily rendered thermoplastic, and is generally handled with less difficulty than Perbunan. In all other respects its behaviour follows very closely that of the parent material.

Moll, Howlett and Buckley have shown that for Buna-N materials resistance to swelling in solvents is greater as the proportion of acrylic nitrile increases. On the other hand the cold crack temperature becomes worse, i.e. the temperature of cracking becomes higher.

Hycar. Hycar is the trade name for a group of synthetic rubbers which have been available since 1939, made by the B.F. Goodrich Co. The latter company manufactures articles from these synthetic rubbers which are sold under the name of Ameripol. Hycar OR-15 is a 45 acrylic nitrile 55 butadiene compound, while Hycar OR-25 is a 35/65 combination. The leading type is Hycar OR, a synthetic rubber based on butadiene and acrylic nitrile. It contains about 25 per cent. of the latter. It is an amber, crêpe-like material whose specific gravity is 1·00. It has a pleasant odour. It can be blended with rubber and reclaimed rubber in all proportions, with neoprene, Thiokol, polyvinylchloride, etc.

Almost everything that has been said about Perbunan can be applied equally well to Hycar OR. Oil resistance of the latter is claimed to be superior. Oil resistance, heat resistance, and the resistance to oxygen, are the outstanding advantages.

The same difficulties are encountered in breaking it down and compounding, and similar methods are adopted to overcome these difficulties. For example, only small batches can be handled on the mixing mill.

The difficulty of compounding Hycar OR is reflected in the use of larger proportions of plasticizers. Similar types of plasticizers and softeners as these used with Perbunan are equally effective. Thus esters, ethers, and ketones used as plasticizers for lacquers and plastics, such as dibutyl phthalate, tricresyl phosphate, etc., are very effective with Hycar OR. They yield snappy resilient materials. The usual run of softeners used with natural rubber, e.g. pine tar and coumarone resins, etc., are also extremely useful. Suitably selected plasticizers can, however, be added in large quantities without unduly affecting vital properties.

The behaviour of filling materials appears to follow more closely the behaviour in natural rubber than in Perbunan. Optimum tensile

TABLE 151. EFFECT OF SOFT COAL TAR ON HYCAR OR COMPOUND [7]

	Parts by weight.		
Hycar OR	100	100	100
Zinc oxide	5	5	5
Phenyl-β-naphthylamine	1	1	1
Benzthiazyl disulphide	1	1·25	1·5
Sulphur	1	1·25	1·5
Channel black	50	50	50
Stearic acid	1	1	1
Soft coal tar	5	25	50
Vulcanized for 20 minutes at 310° F.			
T_B lb. in.^{2}	3,500	3,200	2,400
E_B per cent.	450	600	675
Shore Hardness	74	70	66
Percentage volume change immersed in			
Hexane 48 hours at 25° C.	+3	0	0
Circo light oil 48 hours at 100° C.	+6·1	0	−8·4

strength is obtained by the use of channel black in loadings comparable with those used with rubber. Soft blacks yield excellent all-round stocks. Fillers such as clay, magnesia, iron oxide, calcium silicate barytes, whiting, etc., give products having good tensile strength. With these fillers high permanent set is obtained while in general the resilience is adversely affected, the products being dead and loggy. They also help to reduce the cost of the mix.

Drogin [4] studied the behaviour of black filled in Perbunan and Hycar OR in relation to smoked sheet. It is extremely interesting to notice the divergence of properties from similar compounds, although both Perbunan and Hycar OR are in the Buna-N class of materials.

TABLE 152. SEMI-REINFORCING BLACK IN PERBUNAN, ETC.[4]

	Smoked sheet	Perbunan	Hycar OR
Plasticity (mm.)	153	454	420
Extrusion (seconds)	1·2	11·1	23·7
Modulus, at 200%	1000	1385	1800
Tensile strength (maximum)	2840	2950	2850
Elongation at break	420	315	260
Shore hardness	65	70	75
Tear resistance	1165	475	400
Abrasion resistance	175	17	4
Percentage rebound (*a*)	53	43	17
Heat build-up, average temp. ° F., (*b*), (*c*)	130°	171°	161°
Percentage compression	4·3	2·8	1·1
Percentage set	4·0	2·4	2·0
Shrinkage	4·8	6·7	3·8
Electrical resistance (*e*)	23 × 10^3	3 × 10^8	4 × 10^8

TABLE 153. COMPOUNDS EMPLOYED [4]

	Pure gum		Reinforcing black		Semi-reinforcing back	
	Rubber	Perbunan or Hycar OR	Rubber	Perbunan or Hycar OR	Rubber	Perbunan or Hycar OR
Elastic	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	3·5	1·5	2	1·5
Altax	1	1	1	1·25	0·65	1·25
Pine tar	—	—	3	3	—	1·5
Paraflux	—	—	—	3	—	1·5
Sulphur	2	2	2·85	2	2·85	2
Dixie 20/Kosmobile	—	—	—	—	60	60
Kosmobile 77/ Dixiedensed 77	—	—	50	50	—	—

Sulphur is necessary for vulcanization, being used in rather lower quantities than in rubber. The usual run of accelerators are employed performing the same function as in natural rubber, slightly higher amounts being needed. Thiuram accelerators giving off free sulphur are likewise employed for preparing heat-resisting products. As with rubber careful control is necessary in order to avoid scorching.

TABLE 154. REINFORCING BLACK IN PERBUNAN AND HYCAR [4]

	Smoked sheet	Buna-N	
		Perbunan	Hycar OR
Plasticity (mm.)	245	454	467
Extrusion (seconds)	2·2	11·3	24·2
Modulus at 300%	1450	2160	2300
Tensile strength	4075	3600	4030
Elongation	565	415	450
Hardness	64	70	75
Tear	1360	328	381
Rebound	48	40	18
Abrasion (*a*)	202	19	4
Heat build-up ° F. (*b*)	137°	181°	183°
Shrinkage (*d*)	2·9	7·7	6·8
Electrical resistance (*e*)	$7·5 \times 10^6$	21×10^7	11×10^7

TABLE 155. COMPARISON OF RUBBER AND BUNA-N[4]

(Rubber properties rated at 100 in each case)

	Pure gum			Reinforcing black			Semi-reinforcing black		
	Smoked sheet	Perbunan	Hycar OR	Smoked sheet	Perbunan	Hycar OR	Smoked sheet	Perbunan	Hycar OR
Plasticity	100	39	40	100	34	60	100	34	36
Extension	100	—	—	100	19	9	100	11	5
Modulus	100	—	—	100	114	159	100	139	180
Tensile	100	25	40	100	88	99	100	104	100
Elongation	100	67	73	100	74	80	100	75	62
Hardness	100	129	129	100	109	117	100	108	115
Tear	100	30	35	100	24	28	100	41	34
Abrasion	100	—	—	100	1055	5950	100	1030	4380
Rebound	100	81	37	100	83	38	100	81	32
Heat build-up %	—	—	—	—	44	46	—	41	31

Mercaptobenzthiazole accelerators are found to be quite effective. Dibenzthiazyl disulphide is as useful for Hycar OR as it is for rubber stocks, there being little fear of scorching during processing. Zinc oxide and litharge has been found to be an excellent accelerator for Hycar OR mixes. Five parts of zinc oxides and 10 parts litharge are normally used.

TABLE 156. HYCAR TYRE TREAD MIX

	Parts by weight.	
Hycar OR	100	100
Stearic acid	0·5	0·5
Plasticizer	25	25
Benzthiazyl disulphide	1·25	1·25
Channel black	55	55
Zinc oxide	5	5
Anti-oxidant	1	1
Sulphur	2·5	3
Cure at 45 lb./in.^{2}	30 minutes	20 minutes
T_B lb. in.^{2}	2900	2900
E_B per cent.	577	610

Since Hycar OR is supplied with 2 per cent. of phenyl-β-naphthylamine, normally there is no necessity for further additions of anti-oxidants. Thus in a tread type of mixing the sulphur content would be 1·25, and a typical accelerator addition 1·25 parts benzthiazyl disulphide.

The outstanding property of Hycar OR is the excellent resistance to a wide variety of solvents. In this respect it is superior to Perbunan, especially as regards the newer types of aviation petrol. It is very little affected by aliphatic solvents, oils, by alcohols, water, etc. The performance is greatly dependent upon compounding. The behaviour of various compounds has been described by Garvey, Juve, and Sauser.[8]

TABLE 157. RECIPES OF COMPOUNDS STUDIED [8]

Compound	A	B	C	D	E	F	G	H	I
	Tread	Low set	Gasoline hose tube	Heat resistant	Soft stock	Clay loading	Soling	Pure Gum	Fast-curing
Hycar OR	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0
Zinc oxide	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0
Age resister	—	—	—	5·0	—	—	—	—	—
Mercaptobenzthiazole	—	—	—	3·0	—	—	—	—	1·5
Benzthiazyl disulphide	1·25	1·0	1·0	—	1·5	1·5	1·25	1·0	—
Tetramethyl thiuram disulphide	—	—	—	3·0	—	—	—	—	—
Di-ortho tolyl guanidine	—	—	—	—	—	—	—	—	0·25
Crude lauric acid	1·5	1·5	1·5	1·5	—	—	—	1·0	—
Sulphur	1·25	2·0	1·0	—	1·5	1·5	1·5	1·0	1·25
Channel black	50·0	—	—	50·0	—	—	75·0	—	50·0
Gastex	—	50·0	100·0	—	—	—	50·0	—	—
P. 33 black	—	—	—	—	25·0	—	—	—	—
Clay	—	—	—	—	—	75·0	—	—	—
Soft coal tar	3·5	—	—	10·0	—	—	25·0	—	20·0
Dibutyl phthalate	—	20·0	20·0	—	50·0	20·0	—	—	—

Time of cure, 45 minutes at 155° C.

They are affected by aromatic hydrocarbons such as benzene, by many chlorinated solvents (except carbon tetrachloride), by acetone and other ketones.

The tensile strengths obtainable are comparable with those obtained in rubber compounds, while elongations are similarly dependent upon the amount of fillers.

Hycar OR products have good resistance to heat, especially when compounded specially for this purpose. They can be used at 300° F. and in a few limited applications, even at 400° F. They tend to become harder and tougher under such conditions, in contrast to the behaviour of rubber. Their behaviour at low temperature is inferior to that of rubber compounds as they tend to become leathery

at − 10° C. Elastic properties may be maintained by the use of plasticizers such as dibutyl phthalate, in which case a temperature of − 35° C. can be reached before becoming leathery. The crack point is said to be as low as − 50° F.

The resistance to ageing is also superior to that of rubber.

TABLE 158. EFFECT OF SOLVENTS ON HYCAR OR [8]

Solvent	Percentage volume change of compound								
	A	B	C	D	E	F	G	H	I
	48-hour immersion at room temperature								
Hexane	1·5	0·0	0·0	3·0	−6·1	0·0	0·0	4·5	0·0
Benzene	127·4	104·8	86·1	102·4	114·7	90·7	76·3	209·6	135·4
Carbon tetrachloride	36·8	26·0	23·4	36·8	11·7	20·8	25·1	64·3	36·8
Acetone	176·0	151·5	144·9	234·5	191·7	147·4	105·1	345·1	224·6
X-70 gasoline	4·5	1·5	3·0	4·5	−9·2	3·3	2·2	9·2	3·7
95% ethanol	9·2	3·0	3·0	7 6	−10·0	3·0	3·0	14·9	7·6
Distilled water	0·0	0·0	3·0	1·5	0·75	0·0	0·75	0·0	1·5
S.A.E. 20-W oil	0·0	−1·5	0·0	0·75	−6·1	−0·75	0·0	0·0	0·0
95% kerosene +5% benzene	0·75	0·0	0·0	1·5	−4·5	0·0	0·0	2·2	0·0
	48-hour immersion at 100° C.								
Circo X light oil	9·2	0·0	0·0	5·3	−19·1	0·0	4·5	14·9	4·5
95% kerosene +5% benzene	11·6	0·0	0·0	6·1	−17·4	18·2	6·1	0·0	4·5

In general, the applications are very similar to those of Perbunan. It is widely employed for gaskets, packings, petrol tube, and generally where petrol, oil, or heat conditions are likely to be encountered. Hycar OR compositions may be bonded to metals by the technique described for Perbunan using chlorinated rubber as adhesive.

Garvey and Sarbach [7] have described how ebonite can be made from Hycar OR-15. They suggested the following compositions:

TABLE 159. COMPOUND SUITABLE FOR ACCUMULATOR CASE

Hycar OR	100	—
Sulphur	40	For vulcanization
Clay	50	For processing, moulding and acid resistance
Cumar	10	To confer tack and smoothness
Dioctyl phthalate	10	
Dibutyl metacresol	6	

TABLE 160. COMPOUND FOR HIGH-QUALITY SMALL MOULDINGS

Hycar OR	100	—
Sulphur	40	—
Zimate	2	Accelerator
Iron oxide	75	For processing, high tensile and moulding
Oil	15	To confer tack and smoothness
Tricresyl phosphate	5	
Rosin	5	

Chemigum. Chemigum N is the name for a series of elastomers made by the Goodyear Rubber Co.

Chemigum N3 is a copolymer of 55 parts of butadiene and 45 parts of acrylonitrile, contains 2 per cent. of phenyl-β-naphthylamine, and has a specific gravity of 1·00. Vulcanized compounds prepared from it are characterized by high tensile strength and low compression set.

Chemigum N3NS is like N3 but contains a non-staining antioxidant and therefore is of use where a highly resistant non-staining rubber is desired.

Chemigum N4NS has a lower proportion of acrylonitrile, being prepared from 70 parts of butadiene and 30 parts of acrylonitrile. It also contains a non-staining antioxidant and has a specific gravity of 1·02. When vulcanized it exhibits good resistance to oil, a moderately high tensile strength and a fair degree of flexibility at low temperatures. It is an all-purpose type and is used for applications where some oil resistance and general all-around good properties are desired.

Chemigum Latex Type 200 has the same polymer composition as Chemigum N4NS, contains approximately 55 per cent. solids, and is of use for the preparation of dipped goods where oil resistance is required.

Butaprene N Rubbers. A modified copolymer of butadiene and acrylonitrile known as Butaprene N is produced in four standard types by the Firestone Rubber Co. Products made from the Butaprenes have operated successfully at temperatures ranging from - 70° F. to 300° F.

Type NXM gives products with high tensile strength, excellent elongation and low compression set. They have maximum resistance to aromatic solvents, naphthenic oils and chlorinated hydrocarbons. Accordingly they are useful in such applications as gaskets, packing, seals, sleeves and diaphragms.

Type NL is used where oil resistance must be combined with flexibility at low temperatures, for instance, in uses such as gaskets, seals, packing and hose operating in coolants, hydraulic fluids and lubricating oils.

Type NF is used where maximum resilience and resistance to stiffening at low temperatures are required, and where shrinkage in high aniline point lubricating oils is undesirable.

Type NAA needs no plasticizer and therefore can be used where

the leaching out of any plasticizer would (1) cause loss of seal because of shrinkage in rubber volume, or (2) affect the taste or flavour of a liquid in contact with the rubber.

Product Compounding. The Stanco Company, which has taken a leading part in the evolution of the Perbunan class of material, has formulated the following typical mixings as suitable for a number of leading products. They market three types—Perbunan 18, 26 and 35 containing varying proportions of acrylic nitrile.

TABLE 161. SPONGE

	Soft	Medium	Firm
Perbunan	100·0	100·0	100·0
Zinc oxide	5·0	5·0	5·0
MBTS	1·0	1·0	1·0
Sulphur	2·0	2·0	1·75
Sodium bicarbonate	10·0	10·0	10·0
Dibutyl phthalate	80·0	80·0	—
Whiting, precipitated, surface treated	24·0	24·0	—
Stearic acid	1·5	—	10·0
Alum	11·8	13·3	—
Thermax	—	—	25·0
Tricresyl phosphate	—	—	50·0
Antioxidant	—	—	2·0
Vulcanize, 55 mins. at 287° F.	—	—	—

SOFT STOCK

Perbunan, 100; brown factice, 50; stearic acid, 0·5; sulphur, 2; zinc oxide, 5; MBTS, 2; SRF black, 20; methyl ricinoleate, 100.
Vulc. 120 mins. at 287° F.: T_B, 300; E_B, 750; H, 15; Resil., 53.

TABLE 162. HOSE COVER AND TUBE

	Cover	Tube
Perbunan	100	100
Zinc oxide	5	5
Stearic acid	1·5	1
MBTS	1·25	1
Sulphur	1·5	2
Thermax	50	150
Micronex	50	—
DPG	—	0·3
Sunproof wax	2·5	—
Coal-tar softener	25	—
Dipolymer oil	—	20
Cumar P.25	—	20
Vulc. 45 mins. at 287° F.: T_B	2030	1300
E_B	700	740
H	62	55
Volume increase, per cent., 24 hours in aviation fuel at room temperature	15·2	13·5

Table 163. Petroleum Fuel Resistant Stocks

Perbunan	100	100
Zinc oxide	5	5
Stearic acid	0·5	0·5
MBTS	1	1
Sulphur	2	2
Thermax	130	130
Dibutyl sebacate	35	17·5
Tributoxy ethyl phosphate	—	17·5
Vulc. 30 mins. at 287° F.: T_B	1445	1430
E_B	630	620
M_{300}	630	760
H	50	51
Percentage volume increase, 24 hours in 40 per cent. aromatic fuel	27·9	25·5
Percentage volume increase, 168 hours in 40 per cent. aromatic fuel	27·4	24·5
Vulc. 120 mins. at 287° F.: T_B	1430	1390
E_B	460	450
M_{300}	900	970
Hardness at temperature (° C.) of: 22	53	51
0	54	54
−10	54	57
−20	59	59
−30	68	63
−40	82	72
−50	100	92

Table 164. Friction Stocks

Perbunan	100	100
Zinc oxide	139	139
Stearic acid	0·75	0·75
MBTS	1	1
DPG	0·25	0·25
Sulphur	2	2
SRF black	5	5
Heavy pine tar	15	35
Dipolymer oil	35	15
Vulc. 15 mins. at 287° F.: T_B	1010	860
E_B	1100	1100
H	25	30
Vulc. 30 mins. at 287° F.: T_B	1140	1200
E_B	1100	1100
H	25	25
Vulc. 60 mins. at 287° F.: T_B	1170	1250
E_B	1100	1000
H	25	30
Vulc. 120 mins. at 287° F: T_B	1130	1240
E_B	1080	1050
H	25	30
Adhesion, frictioned, A.S.T.M. D413–39, machine method	21	23
Adhesion, skimmed, A.S.T.M. D413–39, machine method	19	20

Note.—High zinc oxide loadings appear to yield friction stocks having higher degree of tack than stocks with corresponding volume loadings of SRF black.

TABLE 165. CALENDER FRICTION STOCKS

		1	2	3	4	(Skim stock)
Perbunan		100	100	100	85	100
Whole-tyre reclaim		—	—	—	30	—
Zinc oxide		5	5	5	5	5
Stearic acid		0·75	0·75	0·75	0·75	0·75
SRF black		50	50	50	50	50
Sulphur		2	2	2	2	2
MBTS		1	1	1	1	1
DPG		0·25	0·25	0·25	—	0·25
Heavy pine tar		25	15	25	15	—
Dibutyl phthalate		25	—	—	—	—
Dipolymer oil		—	35	40	35	20
Cumar P-25		—	—	—	—	10
Scorching, mins. at 227° F.		70	80	90	70	40
Vulc. 30 mins. at 287° F.:	T_B	1360	1350	1120	840	1940
	M_{500}	550	450	220	450	1290
	E_B	810	930	1150	920	710
	H	46	45	39	46	51
Vulc. 60 mins. at 287° F.:	T_B	1470	1630	1210	1040	2030
	M_{500}	600	490	340	530	1200
	E_B	840	970	990	890	680
	H	47	46	42	47	53
Vulc. 120 mins. at 287° F.:	T_B	1130	1460	1240	1060	2190
	M_{500}	—	570	340	570	1430
	E_B	470	860	990	900	720
	H	50	48	42	47	53
Adhesion, frictioned, A.S.T.M. D413-39, machine method		20–25	18–22	21–24	20–23	—
Adhesion, skimmed, A.S.T.M. D413-39, machine method		19–21	20–22	25–28	21–23	—

NOTE 1.—Mixtures of pine tar with dibutyl phthalate or Dipolymer oil produce good roll adhesion, and may be frictioned over a range of temperature.

NOTE 2.—The addition of reclaim improves fabric coverage and tack.

Table 166. General Purpose Compounds of Medium Hardness and Low Polymer Content

Perbunan	100	100	100
Zinc oxide	5	5	5
Stearic acid	1	1	1
MBTS	1·5	1	1·5
Sulphur	2	2	2
Thermal decomposition black	150	150	130
Channel black	—	—	20
Dipolymer oil	15	—	15
Cumar P-25	15	15	15
Bardol	—	15	—
Scorching, mins. at 227° F.	75	60	75
Vulc. 15 mins. at 287° F.: T_B	1190	1225	1130
E_B	850	940	750
H	46	50	53
Vulc. 30 mins. at 287° F.: T_B	1325	1240	1340
E_B	800	750	650
H	48	55	59
Vulc. 60 mins. at 287° F.: T_B	1350	1250	1350
E_B	700	650	500
H	50	53	63
Volume increase, per cent., 24 hours in aviation fuel at room temperature	11·8	11·0	11·2

Table 167. General Purpose Compounds of Medium Hardness and High Polymer Content

Perbunan	100	100	100
Zinc oxide	5	5	5
MBTS	1	1	1
Stearic acid	1	1	1
Channel black	50	75	75
Bardol	7	7	—
Cumar P-25	7	7	—
Sulphur	2	2	2
DPG	—	0·25	0·25
BRT No. 7	—	—	20
Scorching, mins. at 227° F.	greater than 60	greater than 60	60
Vulc. 30 mins. at 287° F.: T_B	3200	3460	3260
M_{200}	500	1340	880
E_B	600	410	510
H	60	74	73
Vulc. 60 mins. at 287° F.: T_B	3220	3570	3360
M_{200}	650	1410	1090
E_B	530	390	480
H	66	75	77
Vulc. 120 mins. at 287° F.: T_B	3360	3640	3210
M_{200}	590	1700	1160
E_B	530	360	440
H	64	75	79
CS	17·7	17·1	23

TABLE 168. GENERAL PURPOSE COMPOUNDS OF MEDIUM HARDNESS

Perbunan		100	100	100	100	100
Zinc oxide		5	5	5	5	5
Stearic acid		1	1	1	1	1
MBTS		1·25	1·5	1	1	1
DPG		—	—	0·25	0·25	0·25
Sulphur		1·5	1·5	2	2	2
Channel black		—	50	75	75	75
SRF black		100	50	—	—	—
Dimethyl phthalate		12	20	—	—	—
Diphenyl phthalate		13	20	—	—	—
BRT No 7		—	—	25	—	—
Bardex		—	—	—	25	—
Dipolymer oil		—	—	—	—	25
Vulc 8 mins at 310° F	T_B	2170	2220	3550	3000	2440
	F_B	370	470	570	650	660
	M_{200}	1200	860	750	380	340
	H	66	62	74	65	63
Vulc 15 mins at 310° F	T_B	2200	2520	3500	3370	2900
	F_B	340	420	520	570	640
	M_{200}	1450	1100	870	600	400
	H	65	63	75	69	63
Vulc 30 mins at 310° F	T_B	2300	2440	3430	3625	3160
	E_B	330	380	530	560	600
	M_{200}	1520	1110	650	580	450
	H	67	65	78	68	65
Compression set, per cent, 400 lb/sq in constant load						
Vulc 20 mins at 310° F		9·2	15·8	14·3	21·2	20·4
Vulc 35 mins at 310° F		6·8	9·3	9·8	12·6	13·3

Table 169. General Purpose Compounds of High Hardness

Perbunan	100	100	100
Zinc oxide	5	5	5
Stearic acid	1·5	1	1·5
Sulphur	2	2	2
MBTS	1·25	1	1·25
Channel black	100	—	100
SRF black	—	175	—
BRT No. 7	40	40	—
Carbonex S	—	—	40
Vulc. 30 mins at 287° F.: T_B	3210	1720	3150
E_B	470	210	430
M_{200}	1100	1570	1530
H	85	80	91
Vulc. 60 mins. at 287° F.: T_B	3220	1760	3170
E_B	440	200	410
M_{200}	1120	—	1510
H	85	86	88
Compression set, per cent., 400 lb./sq. in. constant load	14·5	6·5	13·7
Vulc. 120 mins at 287° F.: T_B	3200	1900	3080
E_B	360	160	380
M_{200}	1330	—	1700
H	85	85	91
Volume increase, per cent, 4 days in a mixture of Varsol No. 1, 85 parts, and benzene, 15 parts, at room temperature	14 5	11 5	21·7

Table 170. Compounds Containing Natural Rubber or Reclaimed Rubber

Perbunan	100	85	90
Natural rubber	—	15	—
Whole-tyre reclaim	—	—	20
Zinc oxide	5	5	5
Stearic acid	1	1	1
MBTS	1	1	1
Thermal decomposition black	150	150	150
Sulphur	2	2	2
Bardol	30	30	30
Vulc. 15 mins. at 287° F.: T_B	1520	1480	1280
E_B	330	280	330
H	72	80	75
Vulc. 30 mins. at 287° F.: T_B	1640	1550	1390
E_B	300	270	300
H	72	80	75
Vulc. 60 mins. at 287° F.: T_B	1660	1625	1460
E_B	300	230	300
H	75	80	75
Volume increase, per cent. 24 hours in aviation fuel at room temperature	6·8	12·1	12·0

Buna-N Latices (Butadiene-Acrylonitrile Copolymers). Buna-N latices have been mainly employed in Germany under the names of Igetex N and Igetex NN. The first American nitrile latices were made available as a step in the emulsion polymerization process for the production of solid butadiene-acrylonitrile copolymer, but later on were made up specifically for latex users. These latices are produced in privately owned plants and exist in a number of variations. Thus Hycar latices having 40 per cent. solids content are available corresponding to the 15 and 25 types. Chemigum latex type 200 corresponds to Chemigum N4NS having 55 per cent. solids content.

Nitrile-type latices at present could best be designated as special-purpose latices with a very high solvent resistance as the most outstanding characteristic of their films. They are stable water dispersions of butadiene-acrylonitrile copolymer usually, but not necessarily, in an alkali soap stabilized system. As with most other synthetic latices, they are composed of small (approximately 0·07 micron) negatively charged particles in Brownian motion. There is little tendency to cream because of the small particle size and small difference in specific gravity between the solid and serum phases. These latices are handled in much the same manner as Hevea and other synthetics with regard to type of dispersions used for compounding and also methods of processing.

Nitrile-type latices are available in different emulsification systems, solids contents and variations in acrylonitrile content of the polymer itself.

Films from nitrile-type latices show general greater gel and film strength than the films of equivalent GR-S latices. Films may be light coloured or darken on use, depending on the type of antioxidant used in manufacture. The solvent resistance which is higher than other synthetic latices is a function of the acrylonitrile content ; high acrylonitrile gives the best solvent resistance. Nitrile type films have a tendency to stiffen at low temperatures. Here again, the stiffening is proportionate to the acrylonitrile content ; high acrylonitrile gives the greater stiffening.

Compounding follows the general line of Hevea rubber compounding, fillers, thickeners and stabilizers all performing similar functions. Ultra-accelerators are effective in nitrile type latices ; therefore low-temperature fast cures may be used.

Nitrile type latices have found application in adhesives, paper and fabric impregnation and coating, foamed sponge, and dipped goods.

Copolymerization Products. Although no information has

been forthcoming about the specific composition of these materials, a lead can be obtained from some of the patents connected with their production.

For example, in one recent patent [19] it was stated that improved rubber-like materials were obtained by the copolymerization of 1 : 3-diolefines such as the butadienes, $CH_2 : CR.CR : CH_2$, and acrylic acid esters of the form $CH_2 : CR.COOR^1$, where R is a hydrogen or an alkyl group preferably but may be aralkyl or aryl, while R^1 is a saturated aliphatic hydrocarbon radical of four or more carbon atoms, with a branched chain, or is an unsaturated aliphatic or araliphatic radical. Polymerization was effected preferably in emulsion at a temperature of about 50° C. in 100–300 hours. Diolefines that may be used include 1 : 3-butadiene, methyl butadiene, and dimethylbutadiene. Esters suitable include numerous acrylates such as isobutyl-secondary butyl-, isoamyl-, 2-methyl and 3-methyl amyl-, 2-2-dimethyl butyl-, and various heptyl esters.

Perbunan and Polyvinyl Chloride Compositions. The Goodrich Co. have developed new compositions of great promise. In contrast to most blends they have recently been able to prepare vulcanizable blends of plasticized vinyl chloride resins with the Hycar type of synthetics, which possess " most of the best properties of each material ". The blends range from 75 parts Hycar + 25 parts of resin to 50 parts of each, and are easily processed by ordinary rubber technique and to yield products serviceable over an exceptionally wide range. The compositions can be extruded, moulded, calendered or spread. The leading properties are : Extreme resistance to sunlight and ozone, increased resistance (to swelling and cracking) to aromatic solvents ; low-temperature flexibility combined with excellent heat resistance, and improved flexing life, tear resistance, resilience and oven ageing. As regards applications the products are claimed to have unusual advantages in relation to coverings for cables and wires ; shoe solings ; hose coverings where resistance to light, solvents, chemicals and heat is required ; extruded parts and mouldings for the motor-car and aviation industries for special purposes ; spinning cots for the textile industry ; grommets, seals ; insulation and cushioning pads where resistance to the influences mentioned above are necessary ; plating racks and tank linings where resistance to corrosives and heat are essential ; roll coverings where oxidation, oils and heat are met (as in continuous metal processing lines), and for special fabric coatings where specific resistant properties are required. Non-vulcanizable blends can also be made, of utility for many purposes, " the oil-resistant rubber acting as a plasticizer for the resins and as such wholly or

partially replacing the usual liquid plasticizers". One advantage in this respect is that the rubber remains in the compounds under conditions which bring about the dissipation (by extraction or evaporation) of liquid plasticizers.

The possibilities are of such importance as to merit closer consideration of the subject.

It should be emphasized that these materials can be produced from any of the available butadiene-acrylonitrile polymers and polyvinyl resins.

Badum[1] and Henderson[10] have described the properties of mixtures of plasticized polyvinyl chloride resins with butadiene-acrylonitrile rubbers. They have many interesting and useful properties. Emmett has made a very close study of the possibilities available in the complementary properties of acrylonitrile-butadiene copolymers and plasticized polyvinyl chloride resins.

Emmett[5] prepared master batches of Geon and Hycar OR-15, varying the proportion. The master batches were blended by mixing the Hycar OR compound, without sulphur, into plasticized Geon on a hot mill at 220° F.–250° F. The batches were cooled to 120°–150° F., and sulphur was added. All compounds were cured at 300° F., and physical tests carried out.

The addition of Geon to Hycar OR effects several marked improvements; the most outstanding are the excellent sunlight and ozone resistance obtained with 20–30 per cent. of the polyvinyl chloride. Resistance to swelling in benzene is also improved.

Tensile strength, 300 per cent. modulus, and rebound are lowered by Geon addition. Compression set is increased in direct proportion to Geon concentration. Elongation reaches a maximum at 20 per cent. Geon, which may be attributed to the combined effect of increased plasticizer and lowered pigmentation.

The addition of Hycar OR to plasticized Geon imparts thermosetting properties with all of their attendant advantages. Hycar OR may also be used as a non-extractable plasticizer for Geon.

Mixing and Compounding. Uncompounded Hycar OR should be well masticated. The Geon must be suitably plasticized. Tricresyl phosphate was selected because of low volatility and mutual compatability with both Hycar OR and Geon. Its resistance to ozone was found to be superior to other ester-type softeners tested.

The cold-milling properties of the mixtures improve in direct proportion to the Hycar OR concentration; conversely the hot-milling properties are improved with Geon addition. A good balance is obtained with approximately 20–40 per cent. Geon.

Precautions are necessary in compounding mixtures of Hycar OR and plasticized Geon. Excessive use of most metallic oxides and salts and of amine-type age resisters and accelerators should be avoided. At elevated temperatures such materials tend to catalyse breakdown of polyvinyl chloride resins and thus liberate hydrochloric acid. Salts and oxides of lead act as stabilizers for polyvinyl chloride.

Sulphur, accelerator (benzothiazyl disulphide, mercaptobenzothiazole, etc.) and activator (litharge in this case) are used approximately in proportion to the Hycar OR in the mixture. The use of softeners and pigments may be varied in the same manner as in Hycar OR to obtain the desired physical properties. The 3 per cent. age resister already present in Hycar OR plus the inherently good age-resisting qualities of Geon 102 should be sufficient protection for almost all uses. Fatty acids aid both in processing and in obtaining the optimum in physical properties.

The curing rates of the mixtures are similar to those of Hycar OR. The curing curves become progressively flatter with Geon addition. Cured articles, in which 25 per cent. or more Hycar OR is present, may be removed from the mould while hot. This represents an advantage over moulded vinyl chloride resins (100 per cent.) which must be cooled in the press before removal.

Geon-Hycar Polyblends. Mechanical admixture is already out of date. Moulton [13] has described how the polyblend of nitrile rubber and polyvinyl chloride is produced in dispersion. The result is an intrinate dispersion of both components as colloidal particles. This dispenses with the lengthy careful mixing procedure.

The newly developed method of producing the dispersion results in a much better product. Originally the principal reason for use of these blends was that in them the Hycar served as a non-migratory plasticizer for the vinyl component. Mill mixing difficulties, however, required the addition of a moderate portion of liquid plasticizer to the vinyl in order to soften it sufficiently for proper dispersing. Another drawback lay in the fact that it seemed necessary to use three separate milling operations to accomplish the blend. The rubber had to be " broken down " ; the vinyl resin had to be heat softened and partially plasticized, and the two components had to be combined. In a polyblend, all of this work is accomplished during the original manufacturing operation. There is no need for liquid plasticizer ; there is no hot mixing to encourage decomposition of the polymers, and an intimacy of dispersion is achieved such as could never be obtained in working with the dry raw materials.

Processing and Properties. The polyblend will form a smooth sheet immediately on a hot or even a cold rubber mill.

Since the polyblend forms a smooth sheet without milling, it differs from rubber and all other rubber-like products in that it does not require a " breaking down " period. It does not suffer the disadvantages of the vinyl resins which have to be shovelled back on to the rolls until they are sufficiently hot to knit into a continuous sheet.

The properties of uncompounded Geon polyblend 500-X-329 are shown in Table 171.

TABLE 171. PHYSICAL PROPERTIES OF UNCOMPOUNDED GEON POLYBLEND 500-X-329

Tensile, lb./in.^{2}	1850
Elongation, %	430
100% modulus, lb./in.^{2}	1100
Hardness, durometer, " A "	94
Crescent tear, lb./in.	320
Specific gravity, 77 F.	1·23
Freeze, A.S.T.M. (5 hours)—passed at 50 F.	

The tensile strength, although not equal to that obtainable with cured rubber or vinyl resin plus liquid plasticizer, is still quite respectable. The hardness value of 94 indicates that, as a plasticizer for PVC, Hycar is not so efficient as D.O.P. This drawback is a minor one in consideration of the non-migratory nature of the plasticizer. If a softer stock is required, it is possible to lower the hardness to, say, – 83 by the addition of 10 parts of D.O.P., or to – 67 by the addition of 20 parts. This is not such a great amount as to give difficulty with plasticizer migration.

Owing to the presence of the rubber polymer it is possible to load Geon polyblends more heavily than other vinyl plastic compositions. Fillers normally used in rubber compounding are usually satisfactory. Pigments known to improve the sunlight and ozone resistance of rubber can be used to advantage. All breakdown catalysts for vinyl resins should be avoided.

Vulcanization. If desired, the rubber component of Geon polyblends can be vulcanized by conventional methods. Vulcanizing agents should be based on the rubber content of the polyblends, which in the case of the current materials is about 45 per cent. Accelerators such as benzothiazyl disulphide (Altax, MBTS, Thiofide) have been found to be satisfactory with the usual sulphur-accelerator ratio. The use of accelerators such as tetra-methyl or tetra-ethyl thiauram disulphide (Tuads, Thiurad, Thiuram M, Tuex), which act as breakdown catalysts for vinyl resin, should be avoided.

TABLE 172. PHYSICAL DATA ON POLYBLEND 500-X-329

	Unvulcanized	Vulcanized
500-X-329	100	100
Sulphur	—	1·5
Altax (benzothiazyl disulphide)	—	1·5
Selenium (selenium diethyldithiocarbamate)	—	0·5
Litharge	—	5·0
Moulded	5 min. at 345° F.	45 min. at 310° F.
Tensile, lb./in.^{2}	1850	3600
Elongation, %	430	330
100% modulus, lb./in.^{2}	1100	1725
Hardness, Shore	70	74

Solutions of polyblends can be prepared using methylethyl ketone as a solvent and operating at room temperature. The following tables summarize the influence of the respective components in polyblends.

TABLE 173. GEON RESIN EFFECT ON HYCAR SYNTHETIC RUBBER

1. Increased flex life—blend may have more than double the life of pure rubber.
2. Increased sunlight resistance.
3. Increased ozone resistance. It has been found that 25 parts Geon with 75 parts Hycar produce a combination with excellent sunlight and ozone resistance. The resistance is improved as the amount of Geon in the ratio is increased and is excellent in the polyblends containing 55 per cent. Geon.
4. Increased flame resistance.
5. Increased abrasion resistance.
6. Increased tear resistance.
7. Raised scorch temperature.
8. Elimination of nerve. The Geon serves as a loading material in the Hycar.
9. Easier processing—shorter mixing cycles.
10. Ability to produce pastel colours.

TABLE 174. HYCAR SYNTHETIC RUBBER EFFECT ON GEON RESIN

1. Plasticizing action. Hycar exhibits plasticizing efficiency equal to about 60 per cent. of that of D.O.P. and similar plasticizers.
2. Elimination of plasticizer migration.
3. Increased elongation.
4. Increased oil resistance—through elimination of extractable plasticizer. This point might also be listed on the previous table since the Geon frequently protects the Hycar against swelling action of Hycar solvents.
5. Higher loading capacity—thus a cheaper compound.
6. Increased tear resistance. The blend exhibits better tear resistance than either component alone.

As has been indicated, it is possible to use the polyblends in either a vulcanized or unvulcanized condition. The characteristics of the vulcanized polyblends are given in the following table :

TABLE 175. EFFECTS OF VULCANIZATION ON GEON-HYCAR POLYBLENDS

Advantages :
1. Increased abrasion resistance.
2. Increased tensile strength.
3. Increased hot tear resistance.
4. Increased solvent resistance.
5. Superior set and cold flow characteristics.

Disadvantages :
1. Decreased flex life.
2. Decreased elongation.
3. Cannot be reprocessed.

It has been found that these nitrile rubbers are compatible with phenolic resins. So that yet another interesting field of activity has opened up.

In compounds of Hycar OR-15 and OR-25 with phenolic resins, greater hardness can be obtained without excessive pigment loadings and consequently with little or no sacrifice of other physical properties. These compounds are more resistant to the effects of high temperatures and oxidation, by virtue of these qualities inherent in the phenolic resin, and have much better low-temperature flexibility than highly loaded compounds of equivalent hardness. For example, the use of 50 parts of a phenolic resin with 100 parts of Hycar OR-25, with normal curing agents, produces a vulcanizate with a Shore hardness of 92, tensile strength of 2600 p.s.i., and an elongation of 300 per cent., retaining its flexibility at $-40°$ F.

With phenolic resin predominating, equally interesting properties can be obtained. The addition of Hycar to the resin imparts flexibility both in moulding and in the finished product. Electrical properties, impact strength and resistance to water absorption are also improved, all other physical properties being maintained or changed only slightly.

REFERENCES

[1] BADUM, U.S.P. 2,297,194/1942.
[2] BAECHLE, G.P. 702,209/1941.
[3] BRUCE, LYLE and BLAKE, *Ind. Eng. Chem.*, 1944, **36**, 37.
[4] DROGIN, *Rubber Age* (N.Y.), 1942, **51**, 483.
[5] EMMETT, *Ind. Eng. Chem.*, 1944, **36**, 730.
[6] GARTNER, *Kautschuk*, 1940, **16**, 109.
[7] GARVEY and SARBACH, *Ind. Eng. Chem.*, 1942, **34**,
[8] GARVEY, JUVE and SAUSER, *Ind. Eng. Chem.*, 1941, **33**, 602.
[9] GERKE, U.S.P. 1,854,186/1932.

[10] HENDERSON, U.S.P. 2,330,353/1944.
[11] KLEBSATTEL, *India Rubber World*, 1940, **102**, 45.
[12] MOLL, HOWLETT and BUCKLEY, *Ind. Eng. Chem.*, 1942, **34**, 1277.
[13] MOULTON, *India Rubber World*, 1947, **116**, 371.
[14] RÖELIG, *Electro. Tech. Z.*, 1938, **59**, 172.
[15] SEMON, *J. Soc. Automobile Engineers*, 1941, **48**, 97.
[16] STÖCKLIN, *Proc. Rubber Tech. Conf.*, London, 1938, p. 434.
[17] —— *Trans. I.R I.*, 1939, **15**, 50.
[18] STÖCKLIN, G.P. 684,936/1939.
[19] Wingfoot Corporation, B.P. 522,931/1939.
[20] C.I.O.S., XXIII-4.

CHAPTER 17

ELASTOMERS—NEOPRENE OR GR-M

Introduction. The first commercial synthetic rubber was neoprene. In the American Government production neoprene is designated as GR-M. The production capacity is now 63,000 tons. It is the best-known and most easily handled synthetic rubber. This made its debut in the United States in 1931, having been developed by the Du Pont de Nemours concern. Neoprene is a polymer of 2-chloro-1,3-butadiene.

$$CH_2{-}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH{-}CH_2 \longrightarrow$$

Chloroprene

$$-CH_2{-}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH{-}CH_2 \left[CH_2{-}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH{-}CH_2{-} \right]_x CH_2{-}\overset{\displaystyle Cl}{\overset{|}{C}}\ CH-$$

Neoprene

The leading figures in the development of neoprene were Nieuwland and Carothers. This fact shows how close is the relationship between plastics and synthetic rubbers, for Carothers was also the genius behind the production of nylon, that amazing series of synthetic resins which have already attained great importance. This mutual interest in synthetic rubbers and synthetic resins is evident in all manufacturing quarters during recent years.

The story of its discovery started in 1925. Du Pont's were seeking a synthetic rubber which would have properties superior to those of rubber. It was already quite clear that natural rubber could no longer satisfy many industrial requirements and they thought that there would be a market for a more expensive material for special purposes. They could not find a starting point. In 1925 they learned that Nieuwland, of Notre Dame University, had been able to produce monovinylacetylene by passing acetylene through aqueous cuprous chloride. This was commercially practicable.

Chloroprene rubber was discovered, as the outcome of the work on the polymerization of acetylene carried out by Nieuwland.[17] Nieuwland discovered that on passing acetylene into a concentrated solution of cuprous chloride, made with the aid of ammonium chloride or salts of amines, and allowing the reaction mixture to stand, liquid polymers of acetylene could be obtained. Of these the trimer, divinylacetylene

($CH_2 : CH.C \vdots C.CH : CH_2$) could most readily be obtained in good yield. This material could readily be polymerized to a synthetic resin.[16] When completely polymerized it gave a clear, colourless resin, distinguished by the possession of a noteworthy resistance to chemical attack and insolubility in all the solvents which were examined. An intermediate polymeric product from divinylacetylene is now on the market under the designation S.D.O. (synthetic drying oil). When applied in films and exposure to the air, it undergoes conversion to the final polymer, which is very resistant to chemical and solvent attack.

Under appropriate conditions of reaction, acetylene treated with cuprous and ammonium chlorides gives monovinylacetylene which is a dimer of acetylene. Vinylacetylene is a liquid which boils at 5° C. It polymerizes readily to form first a viscous oil and finally a hard, resinous solid.

Preparation of Chloroprene. In the capable hands of Carothers [1] and his team of workers, over a period of five years, this yielded the desired material. First they were able to prepare chloroprene, i.e. 2-chloro-1 : 3-butadiene. Chloroprene is a colourless liquid having a characteristic odour not unlike ethyl bromide. It boils at 59·4° C. and has a density of 0·958. This was obtained by treating monovinylacetylene with hydrogen chloride in the presence of cuprous chloride. By analogy with isoprene they called this "chloroprene". The product polymerized spontaneously to yield material like vulcanized rubber.

It was evident that here was their synthetic rubber. But the process of polymerization had to be brought under control. It was found that by interrupting the polymerization a soft resilient rubbery polymer was obtained which resembled natural rubber in many ways. This was polychloroprene, resembling vulcanized rubber.

When kept in the absence of light at room temperature, chloroprene becomes completely polymerized in ten days to a transparent, resilient, elastic mass resembling soft vulcanized rubber. The product has a tensile strength of about 140 kg. per square centimetre and an ultimate elongation of about 800 per cent. Like vulcanized rubber, it cannot be worked on a mill to a smooth sheet, being non-plastic; it swells strongly but does not dissolve in rubber swelling agents. Completely polymerized chloroprene is known as μ-polychloroprene. If polymerization is carried only part of the way, a plastic material is obtained which is analogous to milled, unvulcanized rubber, and which has been designated α-polychloroprene. The α-polymer can be manipulated on a mill much like raw rubber, various materials being incorporated with it if desired. It can then be transformed into the

μ-polymer by heating or otherwise completing polymerization process. The further polymerization of the intermediate, or α-polymer, to the fully polymerized product, the μ-polymer, is analogous to the transformation of milled raw rubber (plastic and soluble) to vulcanized rubber (elastic and insoluble).

It is a most interesting fact from the structural angle, as Sebrell and Dinsmore [19] have shown, that neoprene is the only elastomer which gives an X-ray diagram when stretched, just as rubber does.

When heated it proceeds to the insoluble condition. At ordinary temperatures the process is slow, but at 130° C. the change occurs inside five minutes. The change is accelerated by a number of materials, among them magnesia, zinc oxide, zinc chloride, ferric chloride, and primary aromatic amines such as aniline, benzidine, etc.

Obviously it was a long and tedious process to work out all the conditions necessary for commercial production. In due course this was successfully achieved, and in 1931 neoprene appeared on the market.

Neoprene Production. This is the synthetic rubber which now has a history of nearly twenty years behind it and whose merits may be based on solid experience. Its career had been one of steady but not spectacular progress. It was never set up as a competitor against rubber but merely for use where rubber could not give satisfaction. Production had been confined to satisfy the steadily growing commercial demand.

But in the U.S. War Production Program, annual production of neoprene was aimed at 40,000 tons. Actual productions have been—

	Tons
1939	1,738
1942	8,998
1943	33,648
1944	58,102
1945	45,651
1946	43,529
1947	31,498

There have not been many types of neoprene. The methods of production have been responsible for slight differences in behaviour. As industrial demands arose for these varied types they were brought on to the market to meet the definite need. But fundamentally the material has remained the same. It has always been a straight chloroprene polymer. Only recently there has been a departure from these principles. The latest introductions to the range are based on butadiene copolymers with chloroprene.

Neoprene is now quite generally accepted by the rubber industry, and is regarded as a standard material There has been great consumer

interest, led by the motor industry. Its present status as a standard material in rubber technology is a tribute to its excellent properties.

Neoprene scores over almost every other synthetic rubber inasmuch as its handling presents no difficulties. With minor reservations it can be handled just in the same way as rubber. This is, of course, an invaluable asset.

Neoprene has a very high chlorine content, nearly 40 per cent. As a result it is virtually non-inflammable and does not support combustion. This accounts for many of its applications, notably in the cable industry.

The property about which most has been heard is the resistance to oils and solvents. It is impervious to vegetable oils, mineral oils, greases, etc., being merely slightly swollen by them, without any marked loss of strength. It is almost unaffected by paraffin, hydrocarbons, and many other solvents It is swelled and dissolved by chlorinated hydrocarbons, and by aromatic hydrocarbons.

There is no questioning its superiority over rubber where these agents are concerned. It is incomparably better, and even where neoprene is attacked to some extent, it still retains the greater part of its physical properties.

Neoprene compositions have excellent resistance to chemical corrosion, particularly against strong acids. Thus it is widely used for lining tanks which contain sulphuric acid, hydrochloric acid, acetic acid, etc.

Subsequent Developments. In the early days there were many disadvantages. The material had a strong pungent odour, and poor colour, while the stabilization was not too good. These defects were thought to be due to the presence of small amounts of oily low polymers. With the passing of time, these faults have been almost completely eliminated. New methods of production have been introduced.

For many years most neoprene was prepared in the massive condition, and while improvements were made, it was not found possible to eliminate the disadvantages. This was Neoprene E, the leading type for many years.

The most profound changes have been brought about by utilizing the method of emulsion polymerization. This avoided the production of the varied by-products which cause the obnoxious odour and conferred the poor colour. The change in procedure was in line with developments in other fields of synthetic polymers where precisely similar improvements were being obtained by the same technique. The surprising feature about this is that the general rubbery products and the processing behaviour differed considerably according to the

method of polymerization used. This has given rise to the different types of neoprene. This was followed by Neoprene G, the emulsion polymer, which had little odour, and could be successfully used to make light-coloured products. A still better product is Neoprene GN.

When neoprene became one of the leading features of the Baruch plan it received the designation GR-M. It is produced at Louisville and at New Jersey. GR-M-10 is GR-M which contains 1 per cent. antioxidant and tends to darken on exposure to light.

Neoprene G was in due course superseded by Neoprene GN, a polymer prepared by the emulsion process. This was the type which was adopted for the Government production scheme under the Baruch plan. It was designated as GR-M. It was produced at Louisville and at New Jersey. These successive types each showed improvement in processing characteristics. The latest and best in this respect is Neoprene GN-A, which is the same as GR-M-10.

Present day types of neoprene may be summarized as follows:

Type GN-A. Also known as GR-M-10. This is identical to GN except that it contains a discolouring antiager. This makes it unsuitable for light shades, but improves storage stability considerably and GN-A is therefore recommended in preference to GN for all purposes where colour is not of primary importance.

Type E. A slow-curing type supplied as plasticized creped sheets or slabs of characteristic odour. It is excellent in resistance to high temperatures and conditions of severe flexing. It is not recommended for making films of 0·010 inch or less in thickness, since it sometimes contains minute particles of polymerized neoprene. In thicker sheets these particles give little or no difficulty.

Type KNR. Chemically similar to GN, but it is capable of being softened by milling to a much more plastic state. In spite of this its vulcanizates have about the same hardness and tensile strength as similarly compounded GN. KNR is recommended for cements and spreading doughs, since for a given solids content these are much thinner than those made from any other neoprene, or alternatively less solvent can be used for producing a given viscosity. KNR can also be used for making special plastic compositions which can be cast without the use of solvent.

Type CG. Is recommended for adhesive cements since it (*a*) provides films of high initial cohesive and adhesive strength, (*b*) is capable of vulcanizing at room temperature, and (*c*) provides films which are unaffected by ageing after vulcanization. GN satisfies (*b*) and (*c*), E satisfies (*a*) and (*c*), but only CG satisfies all three conditions. Type CG is harder than other types in the raw state, but plasticizes

readily on the mill. It can be used for blending with GN or GN-A to produce stiffer unvulcanized stocks, but types S or NC are normally recommended for this purpose.

Type AC. Is similar to Type CG and used for the same purposes. Type AC cements are more stable in viscosity than similar cement made from Type CG. Type AC is available in plasticity grades that may be dissolved in solvent without pre-milling.

Type FR. Has greater resistance to sub-zero temperatures than any other neoprene, and will give a freeze resistance equal to or better than natural rubber. FR also gives very low compression and extension set, high resilience and less water absorption than other types. FR stocks need to be loaded to produce tensile strength and elongation comparable to those of GN.

Type S. Is an outstanding type for the production of crepe soling. It is uniformly tough and does not break down during milling. Thus all scrap can be re-worked to produce a satisfactory product. It does not spread and is relatively unaffected by petrol, oil, sunlight or heat. It may be pigmented or extended with fillers. The resistance of types GN and GN-A to collapse during open steam cures can be increased by compounding with a proportion of Type S.

Type NC. This is a general purpose neoprene which in the unvulcanized state is resistant to rapid mill-breakdown and thermal softening. It therefore provides greater latitude than GN in compounding and is advantageous in the manufacture of such products as thin-walled extruded goods which must retain their shapes in the unvulcanized state and during open steam cure.

Neoprene Latex. Polymerization in emulsion form has resulted in the formation of neoprene latex. The solid neoprene is obtained from this by coagulation in precisely the same manner as rubber is obtained from latex. Neoprene latex is used as such. Films may be made and vulcanized. Impregnation, dipping, and similar processes may be carried out.

Neoprene latex was the first synthetic latex to become commercial available in 1932. During the recent war most manufacturers turned to neoprene latex as a good substitute for natural rubber latex. The increased use of the neoprene latex through the war years has brought general recognition of the unusual properties of neoprene latex films, their resistance to sunlight, ozone, heat ageing, solvents and flame. Experience has shown conclusively that neoprene latices should now be thought of as new and unusual basic latices upon which an ever-expanding field of uses could be built. There are now several types available.

Neoprene latices are available in concentrations of 50 and 60 per cent. solids content. They are stable dispersions of polymerized chloroprene having a negatively charged particle in the range of 0·1 micron diameter. Because of their small size these particles show Brownian motion and do not settle out in spite of their high specific gravity (1·25).

For the most part neoprene latices can be handled by methods common to general latex practice. The same procedures as used with natural latex slightly modified to suit the neoprene conditions are satisfactory.

The outstanding properties of neoprene films are their good gel and film strength coupled with good age, sunlight, fire and solvent resistance. Neoprene films show a tendency to stiffen on standing, but can be restored to their former resilience by rewarming. Neoprene films stiffen at low temperatures and show decreased tensile and tear resistance at elevated temperatures. They darken during cure. Ultra-accelerators are not effective in neoprene stocks : therefore, low-temperature fast cures cannot be attained as with natural latex. Vulcanization is usually carried out at higher temperatures, e.g. 150° C.

Neoprene latex films require the presence of a metallic oxide, usually zinc oxide, and an antioxidant for proper cure. Sulphur is not essential, but is sometimes used. Only antioxidants recommended specifically for neoprene should be used, as those effective in rubber are not necessarily effective in neoprene. Because of the tendency for chloroprene to evolve small amounts of hydrogen chloride during ageing, the presence of an acid acceptor such as zinc oxide or other alkaline substance is essential in neoprene compounds especially for use in contact with fabrics. If light-coloured stocks are desired titanium dioxide or other white pigment must be added to the base compound. Fillers, softeners, and thickening agents are added in the same manner and perform similar functions as in natural latex.

Among standard applications of them are dipped goods, latex thread, balloons, latex foam, as coating for hair, fibre and staple fillers for upholstery, as adhesives, and for paper and fibre impregnation and rug and fabric backing. In fact, almost every application to which rubber latex has been put.

Neoprene latex gloves are being used to an increasing extent in the synthetic fibre and petroleum industries because of their superior oil and solvent resistance ; while household gloves find a ready market by virtue of their quality and performance features. Neoprene surgeons' gloves will withstand 125 sterilizations. Neoprene latex thread, in contrast to natural rubber thread, has an extremely flat

curing curve, and normal variations in curing time and temperature will not change its elongation and modulus properties.

Neoprene latex foam sponge matches all the properties of natural rubber foam. In addition it offers other outstanding properties, including flame resistance, sunlight and ozone resistance, superior flex resistance, and excellent ageing properties. In the adhesive field, high-bond strength plus ability to be loaded with low-cost resins and fillers makes neoprene adhesives of real interest to the cement manufacturer.

The various types of neoprene latex available are the following:

Type 571. A general purpose neoprene latex having a solids content of 50 per cent. It has recently been superseded for most applications by Type 842A.

Type 572. Is recommended for adhesive work, as it is equivalent to Dry neoprene Type CG in providing tough films of high initial cohesive and adhesive strength.

Type 842A. This type is superseding Type 571 as a general-purpose latex. It is more stable; dried films have less odour and higher resilience, are softer to the feel and conventional accelerators can be used to speed up the cure. It is suitable for pale-coloured goods.

Type 601. A 60 per cent. dry solids content neoprene latex basically similar to Type 571. Recommended particularly for the manufacture of froth (sponge), moulded goods made by gellation processes, and dipped goods where a coagulation dip process is not employed.

Type 601A. This newly developed type containing 60 per cent. solids represents the same advantages over Type 601 as does Type 842A over Type 571.

Type 700. This is a special latex developed for use as a coating, impregnant and binder for paper. It contains 50 per cent. solids. Type 700 vulcanizates exhibit low modulus and high elongation. Hence, mixtures of it with other neoprene latices may be employed to reduce modulus and improve the soft feel of the resulting products.

NEOPRENE LATEX 571

Solids	50 per cent.
Price	25 cents per lb. (50 cents per lb. on solids basis)
Particle size	0·1 microns
*p*H	11·5
Useful stability life	2 months
Maximum storage life	8 ,,

(*p*H decreases due to splitting off of HCl, and the emulsion breaks due to the formation of metal salts.)

Properties of Neoprene Films from Neoprene Latex 571. Films from neoprene latex are decidedly tackier than films from rubber latex, have greater tensile strength, are elastomeric and resistent to solvents and greases.

Neoprene possesses poor adhesion to smooth surfaces due in part to the poor wetting action of neoprene latex, and also to a lack of specific adhesion for a relatively smooth surface.

Films of neoprene become progressively harder, tougher, and less tacky on ageing when used as adhesives from either latex or solvent solutions. This makes it necessary to use modifying agents with neoprene.

TABLE 176. TYPICAL ADHESIVE COMPOUND

Neoprene Type 571	100 parts
Zinc oxide	5 ,,
Neozone D	2 ,,
FF wood rosin	15 ,,
Abalyn	35 ,,
Aquarex D	0·5 ,,

The vulcanization or curing of neoprene 571 is not carried out with sulphur as might be expected. Metallic oxide is necessary to accelerate the curing or vulcanizing of type 571 films and zinc oxide is by far the most effective accelerator as well as acting as an acid stabilizer. Usually 3 parts of zinc oxide are used to 100 parts of neoprene.

Neoprene undergoes oxidation on ageing and an antioxidant is used in most neoprene adhesives. About 2 parts of antioxidants to 100 parts of neoprene is recommended as an antioxidant.

It has been found that the formula listed above is an effective adhesive for use in sole-laying, toe-lasting, channelling, cementing the welt, folding, and applying duck to the inner sole.

In the formulation, zinc oxide acts as a stabilizer for the HCl splitting off from the neoprene on ageing and also as a catalyst. The neozone D is used as an antioxidant.

The abalyn and resin in the formulation are used to give a definite tack to the neoprene. Abalyn also serves as a means of cutting down the strength of the neoprene film as well as to give desirable softness so that lamination by pressure is instantly effective.

Behaviour of Neoprene E. Among the earlier types neoprene E stands out. It has been superseded by neoprene GN which was the standard U.S. Government manufacture designated as GR-M. Nevertheless, its behaviour is sufficiently interesting to warrant close consideration.

Neoprene E can be handled in much the same manner as rubber. Standard rubber manufacturing plant is eminently suitable. It may

be milled and mixed on ordinary open rolls, or in internal mixers such as the Banbury.

A very important feature is that the full-sized batch as is used for rubber may be handled. In these respects neoprene is far in advance of other synthetic elastic materials, e.g. of the butadiene class, which require a modified technique. Although the raw material is well stabilized, nevertheless it tends to vulcanize spontaneously when heated, and consequently it must be stored under suitable conditions. In normal factory conditions raw neoprene may be stored for periods of at least twelve months. On the other hand, compounded unvulcanized material has a tendency to scorch, and this must be carefully watched.

Neoprene does not require to be broken down in the same manner as rubber. All that is necessary is to reduce it to a thermoplastic condition when compounding ingredients may be added.

Neoprene is quite different from rubber, and consequently the formulation of its compounds are unlike those of rubber. The essential ingredients in processing neoprene are magnesia, wood rosin, and zinc oxide. Zinc oxide is the vulcanizing agent accelerating the setting up processes caused by heat. It corresponds to the use of sulphur in ordinary rubber compounds, and is used in the proportion of 5 parts to 100 parts of neoprene. Ten parts of magnesia are added, and exert a general stabilizing influence tending also to retard the scorching effect promoted by the use of zinc oxide. Ten parts of wood rosin has an all-round beneficial effect on the physical properties of the final product.

The mechanism of the action of these materials is not yet fully understood. In the case of the wood rosin the important factor is undoubtedly the content of abietic acid. Magnesia not only neutralizes any hydrogen chloride that may be formed under the influence of sunlight or oxidizing conditions, but is also found to increase the tensile strength of the product. Litharge can be used where water resistance makes the presence of magnesia undesirable.

The milling of neoprene is carried out at medium temperatures; neither excessively hot nor unusually cold rolls being desirable.

The order of adding ingredients is:

1. Factice (if used)
2. Magnesia
3. Portion of Softeners and Resins
4. Antioxidant
5. Sulphur (if used)
6. Fillers
7. Remainder of Softeners.

Softeners. The use of plasticizers and softeners is of considerable importance in the manipulation of neoprenes. Vegetable oils such as linseed oil, cotton-seed oil, rape oil, castor oil, and mineral oils are also quite generally employed. The various rubber substitutes are also of great assistance in processing. Apart from these the standard range of plasticizers such as tricresyl phosphate, triphenyl phosphate, chlorinated naphthalene, chlorinated paraffin, etc., are also widely used.

Rubber substitutes, notably dark substitute, play a very important part in the compounding of neoprene. Considerable loadings may be used, and greatly assist extrusion and calendering processes, while giving excellent vulcanized materials. Pine tar is almost interchangeable with wood rosin; the other standard rubber softeners are also used to some extent as and where desirable. Coumarone resins have an excellent capacity for conferring tackiness on mixes. Lubricating materials chiefly employed are paraffin wax and stearic acid.

While GR-M will produce pure-gum stocks of excellent quality, they are excessively nervy and cannot be extruded smoothly without the addition of light loadings of pigments and softeners plus extenders, such as factice, which reduce the quality considerably. Unless special care is exercised in compounding, these soft stocks sag excessively during cure.

It must be remembered that GR-M shows a tendency to lose shape during vulcanization.

Filling Materials. Large quantities of fillers are incorporated into neoprene compositions. They serve the dual purpose of lowering

TABLE 177. EFFECT OF FILLING MATERIALS ON NEOPRENE E MIXES [8]

(Cured: 60 mins. at 141° C.)

Parts by weight

Neoprene type E	100	100	100	100	100	100	100	100	100	100
Light calcined magnesia	10	10	10	10	10	10	10	10	10	10
Wood rosin	5	5	5	5	5	5	5	5	5	5
Cotton-seed oil	5	5	5	5	5	5	5	5	5	5
Mineral oil	10	10	10	10	10	10	10	10	10	10
Sulphur	1	1	1	1	1	1	1	1	1	1
Zinc oxide	10	10	10	10	10	10	10	10	10	10
Thermatomic black	—	115	170	230	—	—	—	—	—	—
China clay	—	—	—	—	115	170	230	—	—	—
Whiting	—	—	—	—	—	—	—	115	170	230
T_B (kgs./cm. sq.)	178	125	107	98	74	67	64	66	45	—
E_B %	930	350	250	180	500	193	77	693	600	—
Permanent set %	1	2	3	3	5	6	—	1	3	—
H	31	67	80	93	69	80	91	62	72	83
% swelling in Diesel oil at 70° C.	61	42	31	30	42	38	32	49	41	—

the cost of the products, and also increase the scope of their application. All the materials used in rubber compounding are equally useful in this case.

The most important fillers are in the carbon black class. The hard channel blacks do not exert anything like the same reinforcing effect as in rubber, and since their use introduces processing difficulties they are not extensively employed alone. On the other hand, the softer blacks give a very desirable improvement in practically every property. The hardness, abrasion, and tensile strength are considerably enhanced. In the normal way the largest possible amount of black filler is incorporated purely from a cost angle.

In fact, the successful use of neoprene depends upon the amount of filler added. So far as black fillers are concerned, it has been found that:

(*a*) For a given degree of oil resistance, as large a volume as possible of a soft black (thermatomic black) should be employed for all but the most severe conditions.

(*b*) When service conditions call for a soft stock having a fairly high tensile strength, slightly harder blacks, such as P.33, should be used.

(*c*) When hard stocks with high tensile strength are required, a mixture of soft black with channel black should be used.

For heat-resisting products, thermatomic black is far and away the best.

Among the other common filling materials china clay and zinc oxide show some reinforcing action. Clay, however, yields rather dead products which have high permanent set. Barytes gives slight reinforcement and is perhaps the best filler for light-coloured products.

Vulcanization of Neoprene E. Sulphur is not essential for the vulcanization of neoprene, this function being performed by zinc oxide. It can, however, have very beneficial results. There is evidence that advantageous results are achieved by the use of sulphur in all cases except where heat resistance is the important feature. It has a profound accelerating effect on the vulcanization of neoprene. Singularly enough, the use of above 3 per cent. of sulphur retards any tendency of a neoprene mix to set up during storage. The mechanism of the action of sulphur is not understood, although the inability to extract any of it indicates that there has been some chemical combination. The time for vulcanization of neoprene E materials is 60 minutes at 141° C. or the equivalent.

There is a pronounced plateau effect in the vulcanization of

neoprene so that the material is not particularly sensitive to over-vulcanization.

There has not been much progress in effecting acceleration of the vulcanization of neoprene. A number of materials have been found which profoundly stimulate the setting up in a manner comparable with the use of fast accelerators in rubber. Addition of certain types of phenols are significant in this respect. Among these are resorcinol,

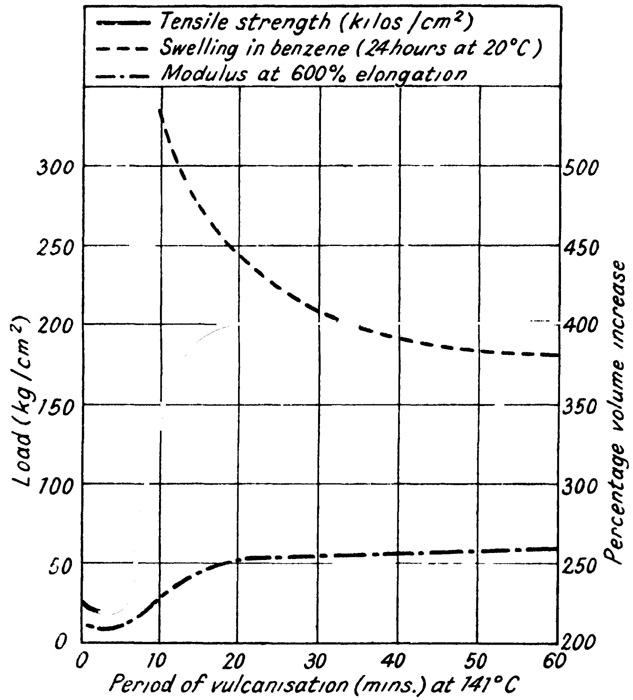


FIG. 82.—Vulcanizing Behaviour of Neoprene.[15]

catechol, and pyrogallol. The use of 0·25 part of catechol to 100 of neoprene profoundly accelerates vulcanization.[15] The effects are shown in the table. Other materials which appear to be capable of exerting a similar accelerating effect include hexamethylenetetramine, tri-ethanolamine, etc.

Processing Neoprene. In general the processing of neoprene compositions subsequent to mixing presents no unusual difficulties. They may be calendered and extruded in the same manner as rubber. Obviously the necessary temperature conditions must be evolved by

trial depending upon the nature of the stock. Heavily loaded stocks are easier to calender and are less sensitive to temperature variations. Neoprene is susceptible to comparatively small temperature variations, so that temperature control is of greater importance even than with rubber. Neoprene GN stocks behave more like rubber than any of the other types of synthetic rubber. Normally neoprene can be

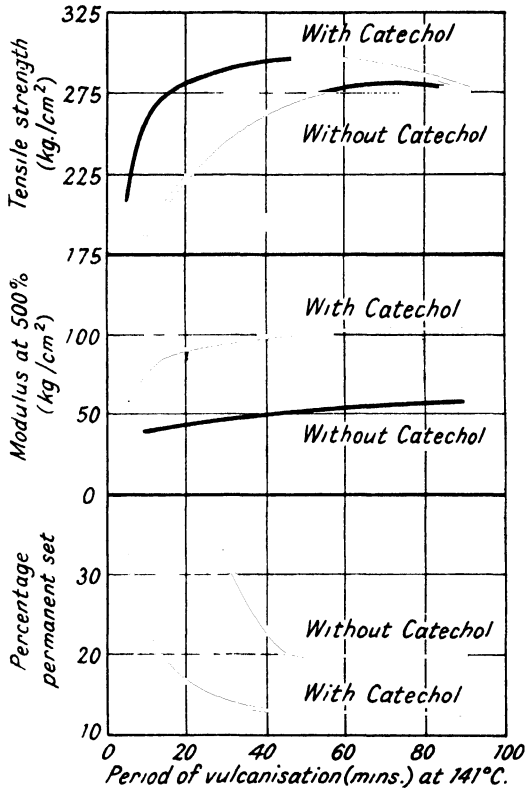


FIG. 83.—Effect of Catechol on Neoprene.[15]

calendered at lower temperatures than rubber. Frictioning and coating are also widely employed procedures with neoprene, and here, too, the behaviour of neoprene G approaches most closely to natural rubber.

For extrusion purposes dark substitute is a particularly useful ingredient, while small amounts of paraffin wax and stearic acid are used for lubricating purposes.

Electrical Properties of Neoprene. Yerzley[22] has illustrated how

the properties of neoprene have continuously improved. He has described the electrical properties of a recent type, neoprene FR, as a typical case in point.

TABLE 178. ELECTRICAL PROPERTIES OF NEOPRENE

Neoprene FR	100	—
Neoprene GN	—	100
Piperidine pentamethylenedithiocarbamate	—	0·1
Phenyl-α-naphthylamine	2	2
Blanc fixe	100	100
Clay	100	100
Semi-reinforcing black	5	5
Process oil	10	10
Paraffin	5	5
Litharge	20	20
Cure at 287° F. (min.)	40	30
Stress at 300 per cent. (lbs. per sq. in.)	275	550
Stress at 500 per cent. (lbs. per sq. in.)	425	650
Tensile strength (lbs. per sq. in.)	700	1125
Elongation at break (percentage)	950	810
Hardness	44	67
Electrical properties :		
D.C. resistivity (ohm-cm.)	$1·2 \times 10^{13}$	$4·2 \times 10^{12}$
Power factor (percentage)	0·9	1·6
Dielectric constant	7·3	8·3
Loss factor	0·066	0·12

Yerzley showed the effect of temperature upon the resistivity of neoprene with the following compound :

TABLE 179. EFFECT OF TEMPERATURE ON RESISTIVITY

	Parts by Weight
Neoprene GN	100
Piperidine pentamethylenedithiocarbamate	0·25
Phenyl-β-naphthylamine	2
Gastex (carbon black)	5
Ground mica	150
Paraffin	5
Shellac	15
Medium-process oil	10
Litharge	20
Cure at 287° F. (min.)	30

Temperature (° C.)	Resistivity (ohm-cm.)
25	$5·46 \times 10^{12}$
40	$1·13 \times 10^{12}$
60	$1·62 \times 10^{11}$
80	$6·01 \times 10^{10}$
100	$1·89 \times 10^{10}$

Conducting Neoprene. At the present time there is a trend towards the use of conductive rubber for a variety of purposes. Electrical conductivity in neoprene is also important, and is attainable by the same means and to the same extent, as for rubber. Yerzley[22] has given the following data based on established commercial products. The data illustrate the range of values attainable with several types of carbon black. Litharge was not used in these formulas since its effect on insulating qualities was not required.

TABLE 180. CONDUCTING NEOPRENE

Neoprene GN	100
Hexamethyleneammonium hexamethylenedithiocarbamate	0·25
Stearic acid	0·5
Phenyl-α-naphthylamine	2
Extra-light calcined magnesia	4
Light-process oil	8
Zinc oxide	5
Carbon black	As indicated
Cure at 287° F. (min.)	30

Type of black	A.C. resistivity (ohm-cm.) 50 parts	100 parts
Acetylene	$2 \cdot 7 \times 10^2$	$1 \cdot 2 \times 10^2$
Soft carbon	$1 \cdot 6 \times 10^8$	$2 \cdot 0 \times 10^7$
Semi-reinforcing	$1 \cdot 0 \times 10^8$	$6 \cdot 7 \times 10^4$
Channel	$8 \cdot 5 \times 10^7$	$1 \cdot 7 \times 10^6$

As a further illustration of the conductivity obtainable, the following data show the trend in a.c. resistivity values with increasing amounts of acetylene black:

TABLE 181. EFFECT OF BLACK ON NEOPRENE

Neoprene GN	100
Hexamethyleneammonium hexamethylenedithiocarbamate	0·3
Phenyl-α-naphthylamine	1
Extra-light calcined magnesia	4
Acetylene black	As indicated
Light-process oil	1
Zinc oxide	5
Cure at 287° F. (min.)	30

Parts of acetylene black	A.C. resistivity (ohm-cm.)
0	1×10^{12}
10	2×10^8
20	9×10^7
30	3×10^4
40	$6 \cdot 4 \times 10^2$
50	$1 \cdot 4 \times 10^2$
75	$1 \cdot 4 \times 10^2$

Solutions of Neoprene. Aromatic solvents such as toluene, benzene, etc., and chlorinated solvents such as trichlorethylene and carbon tetrachloride dissolve neoprene. Doughs made in this way are used for spreading on to fabrics. Solutions are used for dipping. The solutions are less viscous than corresponding rubber ones, and larger amounts of solid can therefore be taken up. The vulcanizing ingredients are added to neoprene on the mill and thin sheets are then dispersed in solvent in the usual solution mixers. No breakdown is required as with rubber.

Small amounts of diphenyl guanidine effectively inhibit any tendency for gelation of neoprene E solutions, but are ineffective with neoprene G. Vulcanization is generally carried out by hot air treatment.

The Bonding of Neoprene to Metals, etc. Neoprene can be very successfully bonded to metals, wood, and other surfaces, a fact of considerable commercial importance. Yerzley [23] has carried out extensive work on this subject, and has described methods for securing excellent adhesion by neoprene. Particularly interesting in this connection is the use of chlorinated rubber cements. By using this it is possible to bond neoprene to most metals and alloys, such as iron, steel, aluminium and its alloys, magnesium, zinc, lead, etc. The technique involves applying coats of chlorinated rubber solution on a perfectly clean surface which has been slightly roughened. Several coats are applied, and the calendered neoprene sheet is rolled on before the final coating is dry. The article is then vulcanized either in steam or in a press. The neoprene mix should be of medium hardness in order to achieve a satisfactory result. In many instances, particularly with magnesium alloys, it is helpful to add 10–15 per cent. of red lead to chlorinated rubber. This process of adhesion can be used to apply neoprene to glass and enamel surfaces.

It is interesting to observe how this technique employing chlorinated rubber is applicable to almost every elastomer.

Neoprene GN. Neoprene GN is the chief type in general use at the present time. This is supplied as unplasticized material, and has to be plasticized as part of the compounding procedure. Vulcanized neoprene GN materials are incomparably superior to earlier types. For example, white stocks and coloured stocks may be prepared which maintain their colour even when exposed to sunlight.

Neoprene GN is best plasticized by the addition of diorthotolyl guanidine often referred to as DOTG. In the ordinary way 0·5 per cent. is required; greater additions result in the formation of soft materials.

Neoprene GN may be handled on mixing mills or internal mixers. It is rather more difficult to compound than other types, and the technique of handling must be carefully studied. In the usual way it should be handled on warm rolls (between 50° and 60° C.) with a fairly tight nip. In these circumstances it forms a sheet in a short time when the plasticizer should be added. It is preferable to add the plasticizer together with some filling material, such as whiting, in order to avoid milling difficulties. Thereafter magnesia is added, and then the main filling ingredients and softeners. Finally zinc oxide is added. In these circumstances mixing normally takes something like half an hour for satisfactory completion. The following mix only takes 30 minutes, at 141° C. for vulcanization:

Neoprene GN	100
DOTG	0·5
Stearic acid	0·25
Light calcined magnesia	4
Zinc oxide	1

No rosin is required for handling neoprene GN. It differs from neoprene G in requiring much less zinc oxide.

The following mixing illustrates the use of a semi-reinforcing carbon black: [8]

TABLE 182.

	Parts by weight
Neoprene type GN	100
Vulcafor DOTG	0·5–1·0
Stearic acid	0·25
Nonox S	2
Light calcined magnesia	4
S.B.I. carbon black	28·8
Zinc oxide	1

Cures at 141° C.	Modulus (Kgs/cm.²) 300%	Modulus (Kgs/cm.²) 500%	T_B (Kgs/cm.²)	E_B %	H
7½ mins.	23	60	144	1010	41
15 „	67	135	216	800	55
30 „	83	163	212	700	57
60 „	86	174	206	600	58

The usual range of additional compounding agents may be incorporated into neoprene GN stocks. The following details illustrate the formulation of mixes suitable for extrusion: [8]

TABLE 183.

Neoprene, type GN	100	100	100
G.810	—	2·5	—
Dark substitute	20	20	20
Light calcined magnesia	4	4	4
Thermatomic black	70	150	175
Mineral oil	10	10	10
Tricresyl phosphate	5	0	10
Neozone D	2	2	2
Nonox NSN	2	2	2
Vulcafor MBTS	0·5	0·5	1
Paraffin wax	0·5	0·5	1
Zinc oxide	5	5	5

PHYSICAL TEST RESULTS ON PRESS-CURED SHEETS

(30 mins. at 141° C.)

Hardness (° Shore)	50	65	75
Tensile strength (kg. per sq. cm.)	110	90	110
Percentage elongation at break	700	290	330
Resilience (% at 50° C.)	58	50	47
Diesel oil figure	39	33	27

Neoprene GN is considered to be particularly good from the point of view of application at low temperatures, and the following mix was found to give a crack point of − 52° C.

Neoprene GN	100
G.810 plasticizer	1·5
Light calcined magnesia	4
Stearic acid	1
Nonox S	2
Lampblack	100
Dibutyl phthalate	50
Zinc oxide	1

The behaviour of neoprene GN in general at low temperatures is favourably influenced by the use of plasticizers such as dibutyl phthalate or dibutyl sebacate.

Outstanding Properties of Neoprene Compounds. Properly compounded neoprene yields materials having physical properties which are in line with comparable rubber products. They are quite as extensible and as strong. Under ordinary conditions the abrasion resistance is better than rubber; but where there is contact with oils or greases neoprene is incomparably superior. This also applies to the other physical properties, for rubber rapidly loses all its resistance whereas neoprene is little affected.

Where special conditions have to be encountered, it is fairly obvious that modifications in the composition of the materials must be made,

Compounding of neoprene for oil resistance in general involves the presence of high loadings of fillers and a minimum addition of softeners which may be leached out by the oils or solvents present.

In general, the processing procedure already described is adopted, and while black fillers are chiefly employed, especially soft carbon blacks, yet for light-coloured mixing barytes, whiting, china clay, zinc oxide, etc., may be employed. The usual softeners are added. In this connection it is interesting to note that it is of advantage to use as a softener the actual oil with which the product may be in contact,

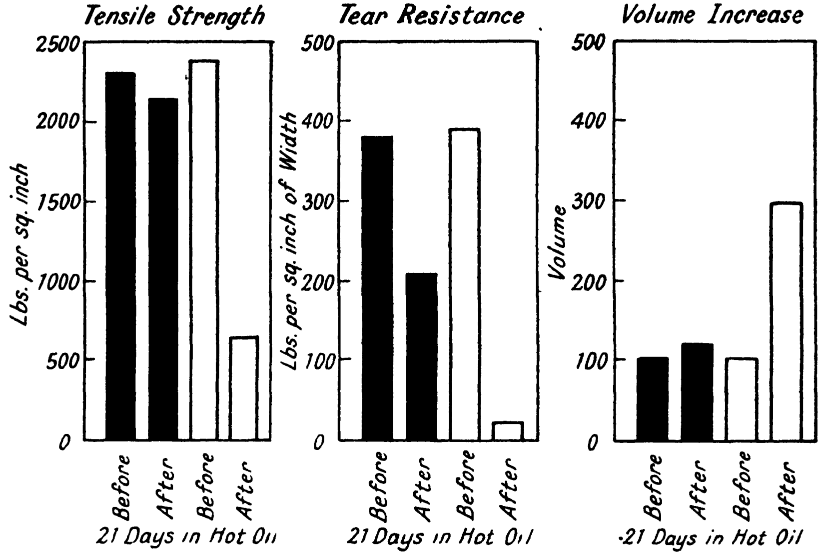


FIG. 84.—Effect of 21 Days' Immersion in Lubricating Oil at 100° C. on Physical Properties of Neoprene (Black Column) and Rubber.[8]

and particularly the quantity which in the ordinary way would be taken up during contact.

For best oil resistance it is also advisable to have a very advanced state of vulcanization. It has been found that additions of soft thioplasts, which are of course highly resistant to the effect of oils and solvents, confer beneficial properties on the oil resistance of neoprene products, particularly in the case of aromatic and chlorinated solvents which do to some extent swell neoprene rather badly. One type that is widely used in this country is known as Vulcaplas. About 30 per cent. of this can be added without interfering greatly with most of the properties of the product.

Recently even better results have been obtained by the use of

another thioplast known as Novoplas A. This is particularly suited for use with neoprene GN. Additions of Novoplas A up to 20 per cent. have little adverse effect on the physical properties. Larger additions do reduce tensile strength and elongation but greatly improve resistance to oils and solvents.

TABLE 184. NEOPRENE E MIX CONTAINING A THIOPLAST [8]

(Cure: 60 mins. at 141° C.)

Neoprene, type E	80
Vulcaplas	20
Rubber substitute	10
Light calcined magnesia	10
Wood rosin	5
Spindle oil	15
Seekay wax A.68	5
Thermatomic black	100
Zinc oxide	5
T_B (kgs./cm. sq.)	80
E_B %	456
H.	61
Elasticity (°Shore)	72

Neoprene has excellent resistance to heat, far superior to that of rubber. This is, however, dependent upon correct formulation of materials.

The following composition is a typical heat resisting type:

TABLE 185. HEAT RESISTING MIX [8]

Neoprene GN	100
Magnesia	4
Nonox NSN	2
Phenyl α-naphthylamine	4
Thermatomic Black	50
Mineral Oil	5
Zinc oxide	15

Cure for 40 mins. at 141° C.

This mixing was still serviceable after 5 days ageing at 150° C. which is very arduous treatment.

Neoprene products gradually become harder and tougher on exposure to heat, in contrast with the degradation of rubber products. In this connection sulphur is always omitted when heat-resisting materials are being made up. Another very vulnerable aspect of rubber is the rapidity with which it is broken down by sunlight, whereas neoprene is virtually unaffected. Oxidation is far less a menace to neoprene than it is to rubber. This is further reflected in

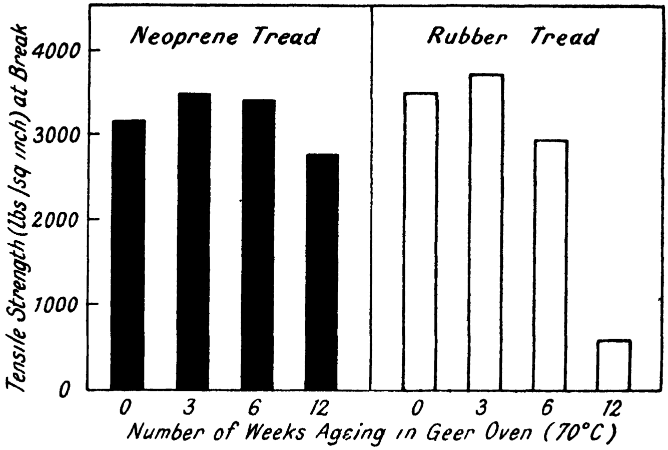


FIG. 85.[8]

the successful manner in which neoprene stands up to ageing, always a bugbear in the use of rubber. This is confirmed both by accelerated tests and by natural life tests. Large amounts of antioxidants are

TABLE 186. BEHAVIOUR OF COMPARABLE NEOPRENE AND RUBBER MIXES IN VARIOUS SOLVENTS AND OILS[6]

Immersed in	Temp. °C.	Compound	Percentage increase in volume		
			24 hrs.	3 days	7 days
Motor petrol	28	neoprene	29	29	33
		rubber	84	84	88
Paraffin (lamp oil)	28	neoprene	14	23	23
		rubber	73	78	78
Paraffin (lamp oil)	100	neoprene	36	36	36
		rubber	142	254	disintegrated
Motor oil	28	neoprene	1	1	1
		rubber	5	7	11
Motor oil	100	neoprene	4	8	10
		rubber	57	108	131
Benzene	28	neoprene	168	172	174
		rubber	113	114	122
Cotton-seed oil	28	neoprene	—	1	2
		rubber	6	8	15
Linseed oil	28	neoprene	1	3	4
		rubber	2	4	7
Turpentine	28	neoprene	50	67	88
		rubber	113	116	135

usually incorporated. Also vulcanization is carried as far forward as possible.

Neoprene compounds are virtually unaffected by sunlight, and are also remarkably resistant to attack by ozone. It withstands the effect of strong mineral acids for long periods of time, and for this reason is used to line tanks, and apparatus used with such acids; naturally ingredients must not be added which will be attacked by the materials with which neoprene will be in contact.

The behaviour of neoprene at low temperatures is of considerable importance at the present time. Neoprene in general does not retain its flexibility to such low temperatures as rubber, becoming leathery

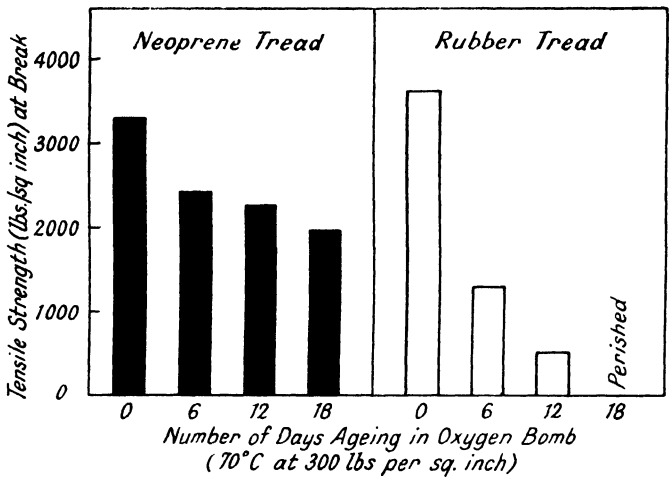


FIG. 86.[8]

at about − 30° C., and brittle at about − 40° C. Nevertheless, by the addition of suitable plasticizers in larger quantities than are normally used for compounding the low temperature range, it may be extended as far as − 60° C., retaining the resistance to oil.

Reclaiming of Neoprene. Large quantities of neoprene are being successfully reclaimed at the present time. The technique is much simpler than with rubber. One method depends upon milling the scorched or vulcanized neoprene with soaps. The general outline of the method is to mill the scorched material, and add small successive additions of the soap, usually a proportion of about 5 per cent is adequate to disperse the neoprene and make it run smoothly. If it is difficult to get the mill started, a small addition of raw neoprene is utilized to act as a compounding medium.

Another method for achieving this is to add small amounts of tricresyl phosphate. It has been found that as little as 2 per cent. does a remarkable job in replasticizing vulcanized scrap neoprene. Small proportions of naphthalene are extremely useful in aiding the reclaiming procedure. The reclaimed material can be used again rather along the lines of rubber reclaim. Additions of raw neoprene aid the compounding, and also the subsequent processing, without greatly affecting the other properties, although it is inadvisable to use very large quantities.

According to Fraser [6] neoprene reclaim may replace as much as 50 per cent. of the new reclaim without greatly impairing the physical properties of medium or low-grade mechanical goods.

The United States Rubber Co.[20] have described an interesting method for reclaiming scrap chloroprene polymers. They stated that neoprene GN is chloroprene polymerized in the presence of sulphur, and neoprene I is a copolymer of chloroprene and an unsaturated nitrile polymerized in the presence of sulphur. Vulcanized and scorched neoprene is reclaimed by heating the finely divided scrap with reclaiming agents and, optionally, suitable oils, swelling agents, or binding agents. To prevent the heat-hardening of the polymer, the heating is done in the presence of a compound, R.COOH, where R is hydrogen or an aliphatic hydrocarbon group containing 1 to 18 carbon atoms in proportions from 2 per cent. to 20 per cent. A long list of the commoner acids is given as suitable for use as the " reclaiming agent ". In a specific example, 10,000 lb. of scrap vulcanized neoprene, 20,000 lb. of water, 1000 lb. of a pine oil fraction, 1000 lb. of rosin oil, and 750 lb. of lauric acid were heated in a digester for 16 hours at about 365° F. and the batch then finished off as in reclaiming natural rubber. The product had a quality comparable with newly compounded neoprene. On the basis that Mooney plasticities of 50–160 at 180° F. indicate easy processing, while 200 and over at 180° F. indicate impossibility of processing, the quality of this reclaim can be judged in that it had a Mooney plasticity of 35 at 180° F. Without the lauric acid, the plasticity was 196. Oleic acid and stearic acid gave plasticities of 20 and 26 respectively, and using 1000 lb. of oxalic, lactic, and sebacic acids, the plasticities were 23, 17, and 25.

With the growing use of neoprene, the problem of reclaiming assumes new forms. How to reclaim when neoprene is mixed with rubber?

The methods for reclaiming of vulcanized ordinary rubber scrap is well known. In all of the economical methods for reclaiming scrap rubber that are in commercial use to-day, high temperatures are used.

These elevated temperatures which range from approximately 300° F. to approximately 400° F. are desirable because they accelerate the reversion of vulcanization and speed up the action of so-called softening agents, and thus contribute to economical plasticization. These higher temperatures are also desirable to accelerate and promote the rapid destruction of fibre where it is present. Because of these facts, equipment that will accommodate these higher temperatures has become standardized and is now in use throughout the rubber-reclaiming industry.

Neoprene is different from rubber in that it does not combine with sulphur to bring about vulcanization and does not undergo reversion of vulcanization through the medium of heat to change it from an elastic to a plastic form. On the contrary, when heat, and especially the higher temperatures referred to, is applied to vulcanized neoprene, it becomes harder. Ordinary rubber-reclaiming conditions are useless for neoprene. For this reason, processes that have been recommended to date for reclaiming scrap vulcanized neoprene have been limited to low temperatures. At low temperatures it is difficult to get sufficient softening action from softening agents without using prejudicially excessive amounts.

Since high temperatures will soften ordinary vulcanized rubber scrap and will harden vulcanized neoprene scrap it is apparent that the usual rubber-reclaiming methods such as the high-temperature digester alkali or digester zinc chloride processes or the high temperature " heater " process cannot be used to reclaim combinations or mixtures of these scraps. This fact has been a source of considerable concern among scrap-rubber reclaimers because the introduction of neoprene into rubber articles causes this scrap to become valueless for further reclaiming use. The accidental mixing of neoprene scrap with rubber scrap would destroy the reclaiming value of otherwise high-quality vulcanized rubber scrap.

The United States Rubber Co.[21] has discovered that sugars, materials rich in sugar, or materials which may be converted into sugars under the conditions of the reclaiming operation will permit reclaiming of scrap vulcanized neoprene by the ordinary methods.

They quoted materials such as sucrose, dextrose, maltose, lactose, laevulose, aldohexoses, aldopentoses, ketohexoses, ketopentoses, di- and polysaccharides, saccharose, polysaccharose starches, and the various crude-sugar mixtures or solutions such as molasses, sorghum, cane-syrup, corn-syrup, honey, etc. Generally from 2 per cent. to 20 per cent. by weight of the reclaiming agent may be used ; 5 to 10 per cent. of sucrose is normally used.

Applications of Neoprene. Neoprene was developed for uses where rubber gave unsatisfactory service or could not be used. As a result it has acquired an enormous spread over industries of every description. It has been used for fittings of every type in motor engines. It has become almost a standard engineering material, being specified wherever oil, heat and abrasive conditions are encountered. It has the odd property of damping out vibration to a much greater extent than rubber. These same properties make it invaluable in aircraft production, its value being further enhanced by its virtual non-inflammability. In the same way it is widely used in shipbuilding. It goes without saying that it is extensively employed wherever oils and solvents are handled, as in oil-refining plants, and for hose and accessories in garages.

It is utilized for many forms of clothing, such as aprons, hoods, boots, etc., in works where corrosive materials are being produced. It is used for making conveyor belts, for handling materials where the influences of oil together with abrasion must be overcome. Printers employ it for a variety of purposes, including their rollers and their plates.

Neoprene is widely used as sponge where oil resistance is required. It is prepared along the lines used in ordinary rubber practice. A gas-evolving agent such as sodium bicarbonate is incorporated as blowing agent.

And so one could go on for a long time cataloguing the innumerable applications throughout the industry.

The electrical properties of neoprene are inferior to those of rubber. According to Yerzley[24] neoprene compounds having just sufficient

TABLE 187. SPONGE NEOPRENE

Neoprene GN	100
Magnesia	4
Zinc oxide	1
Soft black	50
Dibutyl phthalate	25
Liquid paraffin	10
Oleic acid	2
Sodium bicarbonate	10

Cured for 90 minutes at 141° C.

added ingredients to ensure proper vulcanization, at 1000 cycles, had dielectric constant of 7·5, power factor of 0·03 and specific resistance of 10^{12}. It also takes up more moisture. Yet its other properties are so advantageous that it is employed in cable manufacture. Its chief function here is for sheathing cables which have to be non-inflammable,

abrasion resistant, able to withstand oils, solvents, etc. It also resists the influence of ozone to a far greater extent than does rubber.

Little effort had hitherto been made to manufacture ordinary tyres from neoprene. It could not compete on cost with rubber. Also the scale of a manufacture was not large enough for this market. It has been established that tyres can be made which are at least as good as those based on natural rubber. In fact, under severe service conditions such as experienced by truck tyres, neoprene has been found to be definitely superior, and solid tyres based on it are made in the United States.

TABLE 188. NEOPRENE SURGEON'S GLOVE

Neoprene latex 571	100
Zinc oxide	5
Antioxidant	2·0
Accelerator	1·5
Oil	3·0

TABLE 189. NEOPRENE BULBS

Neoprene GN	100
Zinc oxide	10
Stearic acid	3
DBP	9
Calcene	10
Clay	10
Light calcined magnesia	5

Great strides have recently been made in the use of neoprene for adhesive solutions. These have a number of advantages over rubber solutions. These include (*a*) superior ageing characteristics, (*b*) resistance to oil and grease, (*c*) better penetration into porous surfaces and improved anchorage, (*d*) the higher solid deposition per coat. On the other hand they have lower initial strength. Another disadvantage is the inability to use cheap petroleum hydrocarbons, involving either more expensive or more toxic solvents. Earle [5] has made the following comparison in relation to neoprene GN or KN. (See Table 190.)

Neoprene adhesives are being used for bonding neoprene to itself, to wood, metals, fabric, etc. It is also applied for bonding leather, fabric, cork, paper and other materials. The solutions are of great importance for lining tanks merely by painting them with the solution, drying and curing by steam or hot water.

Other Modifications of Neoprene. An interesting example of a modified type is neoprene KN.[16] This produces materials with properties similar to those obtained from type GN. However, type KN differs from other types in that it can be plasticized to a

TABLE 190. NEOPRENE CEMENTS

Property of cement	Rubber	Neoprene
Choice of solvent	Wide	Narrower: insoluble in petroleum solvents
Practical solubility range	Limited	Three to four times more soluble
Initial film strength	Good	Fair
Penetration of porous surfaces	Poor	Excellent
Ageing of uncured film	Poor	Excellent
Ability of properly compounded film to cure at room temperature	Good	Good
Stability of solution	Good	Good
Resistance to oil and grease	Poor	Excellent
General resistance to corrosive chemicals	Fair	Excellent
Dielectric resistance	Good	Fair

much greater extent by the use of chemical plasticizers. The new neoprene is said to offer possibilities in the manufacture of the following types of compositions: (1) heavily loaded compounds; (2) base compounds for cements; (3) compounds containing other types of neoprene; and (4) compounds to be cast in special moulds.

The recommended plasticizers are Latac (hexamethylene ammonium hexamethylene-dithiocarbamate) and DOTG (di-ortho-tolylguanidine). The maximum effect is obtained with 1 per cent. Latac or 4 per cent. DOTG. The former is preferred because of imparting room temperature stability and a rapid accelerating effect at vulcanizing temperatures. At 80° C. untreated type KN has a Williams plasticity of 86, and untreated GN, 245; with 1 per cent. Latac, KN has a plasticity of 12, and GN, 81.

When vulcanized, the following highly loaded compound had a Shore hardness of 100; neoprene type KN, 100; Latac, 2; extra light calcined magnesia, 8; soft carbon black, 250; neozone A, 2; medium process oil, 10; paraffin, 2; and zinc oxide, 20. Yet the unvulcanized compound was sufficiently plastic to flow easily in a curing mould. This compound illustrates the wetting properties of plasticized KN and shows that the extreme plasticization does not lower the hardness of the vulcanizate.

Lightly loaded neoprene KN compounds dissolved in common neoprene solvents (toluene, benzene, xylene, etc.) produce cements having a much lower viscosity than similarly compounded cements made from any other type of neoprene. Obviously, one dip or brush coat of a cement made from KN will deposit a heavier film than will

a cement of the same viscosity made from another type of neoprene. Frequently in the lining of tanks and the covering of metal and other surfaces, a heavier coating than can be economically applied by the use of brushing cements is desired. This can be achieved by trowelling if the solids content of the cement is increased to form a more viscous compound.

When very tacky or extremely plastic unvulcanized compounds are needed KN may be used as the sole basic material in lightly loaded compositions. However, the wide range of plasticity obtainable with mixtures of KN and other neoprene polymers are of interest in the formulation of friction stocks, roll coverings, lathe-cut goods, shoe stocks, and other compounds requiring building tack.

The substitution of KN for other types of neoprene in certain soft-type compounds results in an unvulcanized consistency approaching that of a trowelling compound. This consistency makes it possible to pour the compounds at elevated temperatures, and the lack of volatile solvents eliminates excessive shrinkage. However, such pourable compounds are softer and will display a higher shrinkage than milled compounds. Thus it is possible to shape objects by casting methods, unsuitable for use with normal neoprene compounds; for example, soft-roll coverings can be applied to shafts by casting in a cylinder, or irregular-shaped objects can be vulcanized in plaster of Paris, wood or soft metal moulds.

Casting compositions, pourable at 80° to 90° C. can be prepared, but special procedures are needed in mixing and casting for the removal of entrapped air. Vulcanization is carried out for long periods at low temperature. By modifying the procedure, rubber moulds may be used.

Neoprene Cements. Neoprene types GN (or GR-M), CG, and KNR are suitable for cements for spreading on fabric, for dipped goods, adhesives, and protective coatings for wood, metal, and other materials. The well-known blends of petroleum and naphthenic materials in which the naphthenic or aromatic constituents are about 30 per cent. of the total are widely used solvents for these neoprenes. Blends of benzene or toluene and petrol in ratios of 50 : 50 or 40 : 60 are entirely practical. Neoprene cements at a given concentration of solids are lower in viscosity than rubber cements. This permits the use of cements having relatively high solids per unit of viscosity and means that less solvent may be used to maintain a given viscosity than is the case with rubber cements. Neoprene type CG is outstanding for adhesive cements. Neoprene has a characteristic tackiness that makes it stick to itself and to a very wide variety of other materials such as

raw and vulcanized rubber, GR-S, Thiokol, leather, fabric, wood, and metals.

Other Chloroprene Elastomers. Not all the work on chloroprene rubbers has been carried out in the United States. The other synthetic rubber-producing countries were interested at a very early stage. In the U.S.S.R., for example, one of the leading types has been Sovprene, a chloroprene rubber. The properties of the Sovprene materials were described as long ago as 1935.[12] Frequent references in the literature confirm activity in this direction. Thus, according to Kosloff and Gimpelwitz,[13] the preparation of chloroprene from a solution of vinylacetylene in xylene gave a yield of 53 per cent. as against 32 per cent. by the standard method. A recent account described how Sovprene was made in many grades of varying plasticity which also differ in their processing properties, and showed how these were applied for different purposes.

The I.G. in Germany have taken out numerous patents relating to chloroprene rubbers. For example,[9] they extended the method of catalyzing monovinylacetylene to chloroprene by the use of cuprous chloride by adding alkali metal salts. In another patent [10] they copolymerized chloroprene together with acrylic acid nitrile and styrene, respectively. In addition they described how chloroprene when polymerized in the presence of small amounts of sulphur containing compounds gave superior products. There has been, however, no substantial manufacture of chloroprene rubbers in Germany.

Du Pont de Nemours [4] in one patent also claimed that polymerization in the presence of 0·25 per cent. sulphur gave improved materials. Emulsions containing up to 60 per cent. chloroprene were polymerized at temperatures that could go up to 100° C. The reaction could be stopped at any desired stage by adding a small amount of an inhibitor such as phenyl-β-naphthylamine.

In Japan, Hurukawa and Nakamura [7] have described the preparation of vinylacetylene from acetylene and have developed a synthesis of chloroprene.

REFERENCES

1 Carothers, Williams, Collins and Kirby, *J. Amer. Chem. Soc.*, 1931, **53**, 4197.

2 Catton and Fraser, *Ind. Eng. Chem.*, 1939, **31**, 956.

3 Dales, *India Rubber World*, 1940, **102**, 43.

4 Du Pont de Nemours, B.P. 529,839/1940.

5 Earle, *India Rubber World*, 1942, **106**, 1570.

6 Fraser, *India Rubber World*, 1941, **104**, 152.

7 Hurukawa and Nakamura, *J. Soc. Rubb. Ind. Japan*, 1939, **12**, 103.

[8] Imperial Chemical Industries Ltd., Technical Literature.
[9] I.G., B.P. 471,744/1937.
[10] —— B.P. 512,438/1939.
[11] ISHIGURO, *Rubber Chem. Tech.*, 1933, **6**, 278.
[12] KLEBANSKIĬ, TZYURICK and DOGOPOLSKIĬ, *Bull. Acad. Sci. U.S.S.R.*, 1935, **2**, 189.
[13] KOSLOFF and GIMPELWITZ, *Sintet. Kauchuk*, 1935, **4**, 34.
[14] MALDWYN JONES, *Proc. Rubber Tech. Conf.*, London, 1938, p. 416
[15] NAUNTON, JONES and SMITH, *Trans. I.R.I.* 1933, **9**, 161.
[16] Neoprene K.N., *India Rubber World*, 1941, **104**, 34.
[17] NIEUWLAND, U.S.P. 1,811,959/1931.
[18] SCOTT, *Trans. India Rubber World*, 1929, **5**, 59.
[19] SEBRELL and DINSMORE, *India Rubber World*, 1941, **103**, 38.
[20] United States Rubber Co., B.P. 566058/1944.
[21] —— B.P. 563753/1944.
[22] YERZLEY, *Ind. Chem. Eng.*, 1939, **31**, 950.
[23] —— *Ind. Eng. Chem.*, (anal.), 1937, **9**, 392.
[24] —— *Rubber Chem. Tech.*, 1943, **16**, 699.

CHAPTER 18

ELASTENES—POLYISOBUTYLENE, BUTYL RUBBER, ETC.

EFFORTS at the polymerization of olefines such as ethylene, propylene, isobutylene, etc., have been carried out for many years, mainly with the object of obtaining improved motor fuels. Among the numerous new synthetic products that have resulted from this work, several have already attained considerable importance in the plastic field, and in the rubber field. As might be expected from the lack of a conjugated system of double bonds, all such materials are thermoplastic.

The outstanding commercial polymers of ethylene is the group generally known as polythene and sold as Alkathene, developed by the Imperial Chemical Industries, Ltd. The output here must run into thousands of tons.

Polyethylene is now being made in the United States by the Du Pont Company and by Carbide and Carbon Corporation. The production in 1944 was 9,000,000 lbs., almost exclusively devoted to electrical purposes. There is some evidence, too, that solid elastic polymers from ethylene are being made in the U.S.S.R. This is one of those materials where plastic properties predominate. On the other hand, polyisobutylene as developed by the I.G. Farbenindustrie, and the Standard Oil Development Company, has predominantly elastic properties, although still thermoplastic.

The deliberate introduction of a predetermined number of conjugated double bonds into materials such as polyisobutylene by copolymerization with small quantities of diolefines such as butadiene, has enabled the Standard Oil Development Company to prepare thermosetting synthetic rubber materials—the butyl rubbers.

Styrene is, of course, another olefine. The polymer polystyrene does show very distinct rubbery properties in the upper temperature range, but since it is in no sense elastic at normal temperatures, it is not considered in detail here. In fact its pronounced brittleness is one of its greatest defects which has not yet been overcome by any plasticizing. It is interesting to note also that Buna-S could quite well come into this group of materials, since it is a pure hydrocarbon derived from an olefine (and a diolefine).

All these materials being pure hydrocarbons they are characterized by outstanding electrical properties.

Polythene. Polythene is the generic name given to solid polymers of ethylene. The molecular weight of these may vary from 3,000 up to 50,000.

The best-known product, it is a tough, horn-like, white translucent material which has considerable flexibility. It is very inert and has great resistance to corrosion ; it has outstanding resistance to moisture and by virtue of its being a pure hydrocarbon it has exceptional electrical properties. Although insoluble in all solvents at ordinary temperatures, above 70° C. it becomes freely soluble in benzene, toluene and other aromatic solvents, in chlorinated hydrocarbons, in aliphatic hydrocarbons and in natural oils. It is quite insoluble in water, alcohols, acetone, ether, vegetable oils, etc.

Polythene is unaffected by ultra-violet light and ozone. Nor is it prone to oxidation under ordinary conditions. It has a marked softening point between 100° C. and 115° C. above which it is a viscous fluid. This sudden transition from solid to liquid is in contrast to most thermoplastics. When heated in air it begins to decompose at about 200° C. It burns quite freely.

It is very resistant to concentrated nitric acid and hydrochloric acid even at high temperatures, but is affected by strong sulphuric acid. It is not affected by strong alkalis.

The electrical characteristics are superb, only equalled by polyisobutylene and polystyrene.

TABLE 191. ELECTRICAL CHARACTERISTICS OF POLYTHENE AT 50 CYCLES

Dielectric constant	2·2
Breakdown voltage	1000 volts per mil.
Resistivity (ohms/cm^3)	$> 10^{17}$
Power factor	0·0005

The tensile strength of moulded polythene is of the order of 2000 lbs. per square inch. When extended there is no tendency for retraction which indicates the absence of marked elastic properties, which only become at all marked near the melting point. It has good impact resistance. Oddly enough, it does not suffer appreciably from cold flow until very close to the melting point. The only great disadvantage is the softness, as a consequence of which it can be cut, scratched, or deformed quite easily.

It may be compounded and mixed with other materials on the mixing mill or in an internal mixer at fairly high temperatures. Materials such as rubber, paraffin wax, polyisobutylene, etc., may be

added. Fillers may also be incorporated in quite large volume at the expense of flexibility while making the material brittle.

Polythene may be moulded or extruded or formed into films. It is extensively employed in cable manufacture and for electrical uses.

Polyisobutylene (or Polyisobutene). The class of materials generically known as polyisobutylene (or polyisobutene) has already acquired considerable commercial importance. Chemically they cannot claim any relationship to rubber, or any of the elastomers already described. Yet the high molecular weight products are more rubbery than rubber!

Polyisobutylene is a polymer of isobutylene. This is a by-product of petroleum processing, is obtained in great quantities from "natural gas" and is also available as a by-product in various industrial processes. It is made in the United States from petroleum derivatives, whereas in Germany industrial by-products are the source. The U.S.S.R., too, has rich sources of isobutylene, which are being utilized.

The lower members of the series are viscous fluids which become progressively more solid and rubbery as the molecular weight is increased. Both fluid and solid products have wide industrial application. Commercial materials include those sold as Vistanex by the Standard Oil Company in the United States, as Oppanol by the I.G. in Germany, and as Isolene by F. A. Hughes & Co., Ltd., in this country.

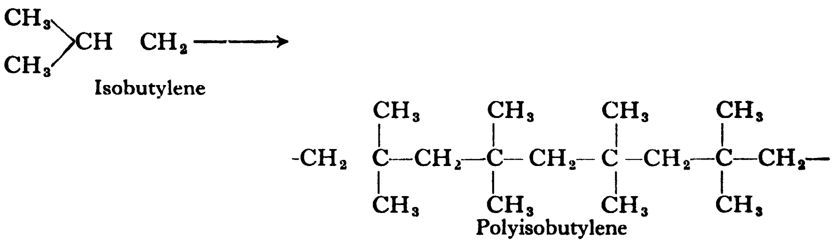


FIG. 87.

Rubber-like polymers of isobutylene are of comparatively recent origin. The other lower polymers had been known for some time. In 1873, Butlerov and Gorianov[3] described the polymerization of isobutylene to yield liquid products, using sulphuric acid or boron fluoride as catalysts. Quite recently Otto and Müller-Conradi obtained products which approached the solid condition, reaching molecular weights up to 10,000. Following upon this, a joint research scheme carried out by the Standard Oil Development Company and the I.G.[22] resulted in the production of high molecular weight com-

pounds, definite rubbery solids. The essential feature for the production of high molecular weight rubbery polymers is to carry out the process at very low temperatures, e.g. below $-50°$ C. Molecular weights of the products ranged from 25,000 up to 400,000. The speed of reaction is extremely rapid often being a fraction of a second.[25]

The manufacturing procedure has been outlined in various patents. For example, isobutylene polymerizes readily in the presence of boron fluoride at low temperatures, below $-10°$ C., and the lower the temperature the higher the molecular weight of the product.

Temperature	Molecular weight
$-80°$ C.	70,000
$-103°$ C.	200,000

Small amounts of impurities in the isobutylene adversely affect the polymerization, reducing the molecular weight to 10,000.

The I.G.[7] have found that small amounts, 0·5 per cent. of materials such as sulphuric acid, nitric acid, formaldehyde, phenol, cresol, and so on, have a notable accelerating effect on the reaction. Added to the isobutylene they shorten the time of reaction, and in many cases considerably increase the molecular weight of the polymer. They also reduce the amount of catalyst involved. According to Mann,[13] an improved process for producing hydrocarbon polymers of high molecular weight from isobutylene comprises adding the olefine in liquid condition to a reaction zone and providing at least three gallons of propane per gallon of isobutylene, bubbling boron fluoride through the liquid and agitating for a short time to bring about polymerization, meanwhile maintaining the temperature below $-20°$ C., by evaporation of a portion of the propane, but maintaining a sufficient portion in liquid condition to produce an easily flowing mass with the polymer, then adding a normally liquid oil to the polymer-propane mixture and removing the propane.

German Manufacture. The Germans used polyisobutylene on a considerable scale. At Oppau production was 400 tons a month, which it was proposed to expand to 1200 tons a month. Isobutanol was made by high-pressure reaction of carbon monoxide and hydrogen. It was then catalytically dehydrated to isobutylene. The product was 98 per cent. pure.

Isobutylene was polymerized in ethylene solution. The ethylene being very pure. It was carried out on a moving stainless steel belt, 12 inches wide and about 20 feet between centres. This was enclosed in a gastight steel shell fitted with windows in which the belt moved at 120 feet per minute. A trough was formed in the surface of the

belt by means of idler pulleys to make space for the reaction mixture. Isobutylene in liquid ethylene was introduced into the trough and a few inches along a solution of boron trifluoride in liquid ethylene was added. A vigorous exothermic reaction took place which caused ethylene to vapourize and left a spongy polymer in the trough. Polymerization was carried to 98 per cent. by the time the end of the trough was reached. The polymer was removed from the pan by scraper blade as it came out of the shell. The vapourized ethylene was collected, liquefied and recycled. The liquid feed to the belt formed a pool about 1 inch deep. Polymerization was practically complete after a travel of about 6 feet along the belt. The polyisobutylene was fed to an extruder which delivered the material as a ribbon about 10 inches wide and $\frac{1}{8}$ inch thick. The liquid was fed on to the belt at minus 100° C., consisting of one part isobutylene and two parts ethylene. The catalyst amounted to 0·001 to 0·003 parts of boron trifluoride. The polymer was milled at room temperature. Low viscosity grades were made by adding di-isobutylene which made the catalyst less effective.

Properties of Polyisobutylene. The lowest polymers, the dimers and the trimers, are clear, free-flowing liquids. As molecular weight increases so does the viscosity. According to Thomas, based on penetration data, the change-over from viscous fluid to elastic solid occurs at a molecular weight of about 27,000. All the products are odourless and tasteless. The specific gravity is about 0·9, varying but slightly with change in molecular weight. Those polymers with molecular weight less than 80,000 have quite low tensile strengths, but when greater than 150,000, the strength is high enough to be measured on tensile testing machines, without any modification.

From the chemical standpoint, polyisobutylene differs from rubber chiefly in being a saturated hydrocarbon, in contrast to the profound unsaturation of rubber. Both are long-chain pure hydrocarbons, and both have a regular distribution of short aliphatic side chains. X-ray examination shows that polyisobutylene behaves very much like rubber. Brille and Halle [2] showed that when stretched it gave an X-ray diagram very similar to that of stretched rubber. The X-ray photographs obtained by Sebrell and Dinsmore [14] illustrate this feature. The inescapable elasticity of polyisobutylene, a fully saturated material, is very significant. For it shatters the many theories which attributed elasticity to forces connected with unsaturation. These are no longer tenable.

The physical properties are closely akin to those of rubber. The commercially available types, such as Vistanex, resemble rubber.

They are colourless, clear materials, very rubbery to the feel. They are much less thermoplastic than rubber. These characteristics do not become marked to any degree below 100° C. Polyisobutylene can be moulded at about 200° C., decomposing at 350° C. It is, however, profoundly affected by sunlight, which after long exposure tends to break it down and make it very tacky. The action is one of depolymerization and is analogous to what occurs with rubber. There is a loss of strength and elasticity in each instance. The use of small amounts of fillers, notably carbon black, greatly inhibits the influence of light.

An outstanding property of this material is the exceptional resistance to corrosive influences, which is almost unequalled. It withstands, almost indefinitely, the effect of virtually all concentrated and dilute acids, with the exception of nitric acid, to which polyisobutylene succumbs only after long exposure. Above temperatures of 80° C., it is however attacked by strong sulphuric and nitric acids. The same degree of resistance extends also to concentrated and dilute alkalis.

Oxidizing agents have no effect upon polyisobutylene. Even ozone has no effect upon it, a property which is found to be very useful. The resistance to the action of ozone is of considerable importance. By contrast the effect on rubber is devastating. This is attributed to the double bonds, the unsaturation of rubber, along the lines described by Harries. According to this reasoning, polyisobutylene, a saturated material with no double bonds, should be unaffected by ozone. This is the case. Moreover, it is found that the presence of appreciable quantities of polyisobutylene exerts a profound protective effect against ozone. These high powers of resistance can be directly attributed to the saturation of the molecules.

Polyisobutylene will not, however, stand up to chlorine and bromine. In these cases new products are formed which appear to have intrinsic merits and are being developed.

The solubility of polyisobutylene in solvents is very similar to that shown by rubber. It is insoluble in solvents such as alcohol, glycerol, acetone, etc. The resistance to water is superb, the take-up over very long periods being virtually nil ; in this it is far superior to rubber. It swells in fats, greases and oils. It swells and dissolves in petrol, benzene, toluene, chlorinated solvents, etc. Mineral oils, paraffin wax, and similar materials also exert a pronounced solvent action. Nevertheless solutions are far more difficult to make than in the case of rubber. Considerable milling and breakdown of the molecule is necessary to facilitate the preparation of solutions.

The temperature range of the elastic properties is remarkably wide, in fact the greatest known. Sheets do not become brittle even at

− 70° C., nor do they soften and melt together at temperatures as high as 180° C. A very surprising feature is that in spite of the rubbery nature of the material, at ordinary temperatures there is no rebound or bounce. Yet at 100° C. its rebound behaviour is quite as good as that of rubber. Polyisobutylene shares these temperature oddities with polystyrene, which, although brittle at ordinary temperatures, becomes extremely rubbery above 80° C., and with polyvinyl chloride which also shows enhanced elastic behaviour at slightly elevated temperatures.

TABLE 192. EFFECT OF MOLECULAR WEIGHT ON BRITTLE POINT [15]

Material	Approx. wt. mol.	Appearance	Brittle point ° C. (±0·5°)
Polyisobutylene	1,500	Viscous liquid	− 23
Polyisobutylene	10,000	Very viscous liquid-solid	− 50·2
Polyisobutylene	100,000	Elastic solid	− 50·2
Polyisobutylene	200,000	Elastic solid	− 50·2
Polyethylene	Low	Soft waxy	− 15
Polyethylene	High	Tough, waxy, but hard	− 68·5

The electrical properties are outstanding characteristics of polyisobutylene. They are equalled only by the other pure hydrocarbon plastics polystyrene and polythene. The power factor is extremely low throughout a very wide range of temperatures, the dielectric constant is low, while the insulation resistance is very high. Coupled with the resistance to moisture, it is a superb electrical material, and finds wide application by virtue of this.

TABLE 193. ELECTRICAL PROPERTIES OF POLYISOBUTYLENE [13]

Temperature	Power factor at 800 cycles	Dielectric constant	Specific resistance ohm/cm	Breakdown voltage
20° C.	0·0004	2·3	$>10^{15}$	23 kv./mm.
85° C.	0·0005	2·2	$>10^{15}$	

Processing of Polyisobutylene. The high molecular weight polyisobutylenes are very gristly rubbery solids. Before any filling materials can be added, these must be broken down on a mixing mill or internal mixer. In the early stage on the mill they have much more nerve or kick than rubber. Breakdown is more pronounced at low

temperatures than at high, in this respect resembling the behaviour of rubber. The effect of mastication is to break down the long molecules into shorter ones. At high temperature softening is chiefly a thermoplastic effect and is reversible, so that when the material becomes cold again all the original nerve is recovered. As in the case of rubber, the solubility is greatly affected by this treatment, as is the viscosity of such solutions. The latter property gives a measure of the molecular weight.

TABLE 194. EFFECT OF MILLING ON POLYISOBUTYLENE [17]
(initial molecular weight 200,000)

Time of milling (minutes)	Maximum temp. (° C.)	Final molecular weight
5	52	163,000
10	66	158,000
20	93	156,000
35	115	144,000

Polyisobutylene has a remarkable capacity for taking up filling materials. Loadings of 1000 per cent. and more are not only possible, but offer little difficulty, and give quite attractive flexible material. As the amount of filler taken up increases, so the temperature of mixing must be lowered; otherwise there are no snags. Polyisobutylene appears to be quite indifferent to the nature of the filler. Any fillers may be added. Only carbon black has any pronounced influence on the properties, increasing the tensile strength and lowering the elastic limit.

Polyisobutylene is compatible with numerous other materials such as bitumens, waxes, oils, resins, synthetic resins, etc. These do not exert any appreciable plasticizing or softening action. In fact, this process is reversed, for in many instances polyisobutylene is used to confer specific qualities on these materials. Thus it reduces brittleness and confers flexibility and ductility at low temperatures, particularly in the cases of waxes, resins, polystyrene, etc. In the case of rubber it confers increased water resistance, enhances the electrical properties, improves resistance to ozone and oxidation, and retards ageing.

Polyisobutylene and its compositions can be handled by the normal methods of the rubber industry. That is to say, they can be extruded, calendered, moulded, etc. But owing to the " nerve " of the material they are much more difficult operations to carry out, worse even than with the elastomers. In the case of the pure materials much higher temperatures are necessary than are normally used with rubber. All these operations are made much easier by addition of compounding ingredients. Mouldings must be chilled before removal from the moulds.

The one outstanding defect of polyisobutylene is the cold flow which

is very pronounced. Subjected to slight load for any length of time there is permanent deformation. The only way to overcome this is to add rubber or an elastomer, although montan pitch minimizes the effect. So far, no satisfactory method of vulcanizing or setting polyisobutylene has been devised that might overcome this defect. Sulphur has no effect, nor has zinc oxide, etc. A reaction does proceed with sulphur chloride, but this is not yet a practical procedure. At any rate at present no change can be produced which will produce the desirable characteristics implied by vulcanization, namely change of solubility, improved mechanical properties, etc.

Applications of Polyisobutylene. The chief applications of these materials have been more in the nature of plastic compositions than direct rubber applications as in the case of the elastomers and other synthetic rubber-like materials.

TABLE 195. SOME PHYSICAL PROPERTIES OF POLYISOBUTYLENE (molecular weight 200,000)

	T_{B}, kg.cm.	E_{B} %	Set %	Rebound Energy	H
Polyisobutylene	60	1000	4	12	35
Rubber mix	160	700	7	66	42
Polyisobutylene + 50% carbon black	105	730	14	8	45
Rubber mix + 50% carbon black	320	450	20	50	65

Straightforward mixes of polyisobutylene and fillers or modifying agents such as clay, whiting, talc, carbon black, cork, coumarone resin, bitumens, etc., have been used for many purposes. Acid-resisting linings, gaskets, packings, insulation, adhesives, sealing compounds, are among typical applications.

The chief application of polyisobutylene has been to modify and improve the properties of rubber articles, notably with regard to resistance to heat, to ozone, and resistance to acid.

Polyisobutylene and rubber are easily miscible in all proportions, the rubber plasticizing the polyisobutylene on the mixing mill. According to Longman [12] the following proportions are found to give the best results:

1. For cable insulation 60–65 parts Vistanex polyisobutylene to 40–35 parts of rubber gives the best ozone resistance to be had with physical properties maintained at an acceptable level.

2. For compounds resistant to acids, alkalis, and corrosive salts, the maximum amount of polyisobutylene possible is recommended. Physical requirements for this type of application are usually low, so

that the rubber content can be set at a much lower percentage approximating to 20–25 per cent.

3. Heat-resisting compounds such as steam hose, conveyor belt covers, etc., usually contain fairly high loadings of carbon black. Actual production has shown that ratios of 50–60 parts of polyisobutylene to 50–40 parts rubber are quite practicable. Singularly enough in these cases additional vulcanizing ingredients must be added for the polyisobutylene, even though alone these ingredients have no effect whatever.

In handling high-molecular-weight polymers produced by the low-temperature polymerization of isobutylene and of mixtures containing isobutylene and diolefins, difficulty has been encountered in maintaining the physical characteristics of the material during mechanical working, and in maintaining the desired high-molecular weight. The polymer materials do not work readily on the mill but show a tendency to break up, to stick to the rolls, and to roll out irregularly in the form of rough, weak and poor sheets. There is a pronounced tendency on the part of the polymer to deteriorate by a breakdown of the molecular weight during treatment on the mill, as well as during subsequent storage or upon standing, particularly at elevated temperatures.

Standard Oil Company of New Jersey [19] overcome these defects by the addition of up to 4 per cent. of sulphur. They found that this addition of sulphur produced a very pronounced smoothing and homogenizing effect upon the polymer or copolymer during working on the mill. It also stabilizes the milled polymer or copolymer against subsequent breakdown of molecular weight from heat and/or storage.

The reason for this effect is not as yet clearly known. It may be that the sulphur is soluble in the polymer since amounts less than about 3 per cent. produce no perceptible change in the appearance of the polymer and show no tendency to " bloom ". The presence of the sulphur greatly reduces the tendency towards tackiness which is otherwise present in the material, especially in material of medium to relatively moderate molecular weight.

It is to be noted that polyisobutylene itself does not vulcanize with sulphur as does rubber.

German Applications of Polyisobutylene. Large amounts were used as waterproofing sheet after being loaded with carbon black or graphite. One such material consisted of 20 parts Oppanol B 200; 67 parts Talc; 5 parts montan wax; 8 parts carbon black.

Loaded sheeting was also used to make gaskets, tank linings, pipe linings, etc. In its application for pipe linings the material was cemented to the metal with a cement consisting of 40 per cent. Oppanol B dissolved in styrene monomer with benzyl peroxide as

catalyst. 5–20 per cent. of Oppanol B 200 were added to paraffin used for waterproofing paper.

Oppanol was mixed with Buna-S to make insulation for high-tension cables having good ozone resistance and weather resistance.

There is already considerable activity in the production of modified derivatives from isobutylene. Thus the Standard Oil Development Company [21] have prepared chlorinated materials. The polymers of isobutylene are chlorinated under conditions of heat and sunlight, the latter being particularly effective. Until a 50 per cent. content of chlorine is reached elastic properties are retained. This material has high resistance to heat and is non-inflammable and has been recommended for cable insulation.

The fully chlorinated material containing 75 per cent. chlorine is a white brittle inelastic powder which shows some promise in the field of coatings.

Polyisobutylene and Rubber. Parker has described a method for estimating polyisobutylene in the presence of rubber. Since polyisobutylene is not co-vulcanized with the natural rubber it is possible to extract it unchanged from a vulcanized sample. The solvent chosen was petroleum ether with a boiling range of 40°–60° C., and the extraction was carried out on the samples after acetone extraction, for 24 hours. Samples examined were: No. 1 commercial polyisobutylene; Nos. 6–8, vulcanizates of mixtures of natural rubber or GR-S, with isobutylene and carbon black. Similar mixings but containing extractable material of the bitumen and factice type instead of polyisobutylene were used as controls, and in these the petroleum ether extraction, after acetone extraction, did not exceed 0·7 per cent.

Table 196 shows the results obtained compared with those calculated from the mix formulae.

TABLE 196. ESTIMATION OF POLYISOBUTYLENE BY EXTRACTION

Mix number	Percentage of Polyisobutylene		
	Theoretical	Pet. ether extract	Difference [a]
1	100	100	0
6	6·0	3·0	− 3·0
7	13·8	14·1	0·3
8	13·8	11·3	− 2·5

[a] Pet. ether extract, minus theoretical value.

The figures show a tendency to be slightly low. It seems a very satisfactory method in view of its greater simplicity and freedom from interference by carbon black.

Butyl Rubber or GR-I. The fact that polyisobutylene possessed elastic properties showed that these were independent of unsaturation, but that vulcanization did hinge on this. The Standard Oil Development Company [23] set out to produce a polymer having only the limited amount of unsaturation required for vulcanization. Upon completion of the vulcanizing operation, such a product should give a rubbery product which was substantially saturated, and should have the chemical stability of a typical saturated paraffin.

This was the principle that eventually resulted in the development of butyl rubber, which is a copolymer of olefine, with a small amount of diolefine. There were obvious economic advantages in being able to use as the main raw material in this process chiefly a simple olefine, such as isobutylene rather than a diolefine such as butadiene.

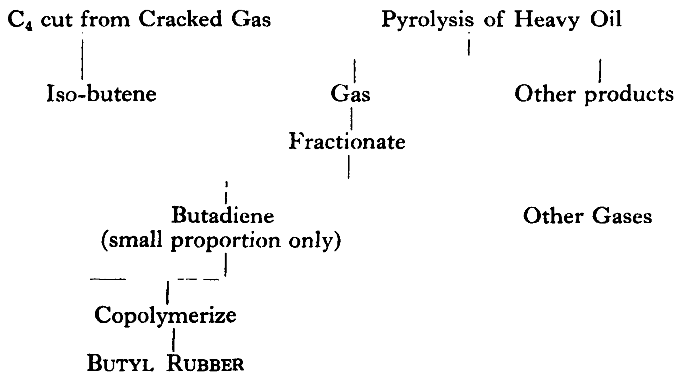


FIG. 88. Butyl Rubber from Cracked Gas.

Butyl rubber or GR-I is already one of the major synthetic rubbers. It is in large-scale production. In 1946 the output amounted to 79,224 tons, and in 1947 it was 76,096 tons.

The term butyl rubber is a generic term, because variation of the types and quantities of olefine and diolefine employed make it possible to obtain products having very different properties, although they all have the one feature in common, that of limited controlled unsaturation.

Butyl rubber in the present instance describes a hydrocarbon product with an unsaturation less than 5 per cent. of that found in

natural rubber, and having a molecular weight between 40,000 and 80,000. It is a soft white material which has no odour or taste. It has the extremely low density of 0·91. It stretches very easily.

Actually a number of types have already appeared and been examined, the degree of unsaturation varying between 1 and 5 per cent. that of rubber. GR-I contains 2 per cent. isoprene.

The method adopted to produce these new copolymers has been described in the patent literature.[18] An aliphatic iso mono-olefine such as isobutylene and a hydrocarbon compound having a conjugated system of alternate single and double bonds and having at least one olefine linkage, e.g. butadiene, isoprene, or styrene, are treated at a temperature below 0° C. with a Friedel-Crafts reagent.

It is desirable that the second constituent be soluble in the other, although the process works when ingredients are dissolved in saturated chlorinated solvents such as carbon tetrachloride.

The Friedel-Crafts catalyst may be boron trifluoride, which is bubbled through, or aluminium chloride which is merely added to the mixture.

In many cases interesting fluid products were obtained. In others rubber-like materials were produced.

As an example 90 parts isobutylene and 10 parts butadiene were cooled to − 78° C. by means of solid carbon dioxide. Boron trifluoride was bubbled through, and after a short time reaction began with the production of a flocculent white solid.

In a later patent [20] The Standard Oil Company modified the type of catalyst, and used a complex of aluminium chloride dissolved in ethyl chloride. By using 10–20 parts butadiene with 90–80 parts isobutylene, they obtained products which had high elasticity and pliability. The reaction was carried out below − 50° C. In this manner they obtained a non-tacky material capable of being vulcanized to give a tough elastic rubber-like product, resistant to oxidation and chemical attack. One point of great interest was that crude mixtures of the reacting compounds may be employed, such as a C_4 refinery cut, which contains a substantial amount of butadiene in addition to isobutylene and normal butylenes.

The limiting proportions are 50 to 5 butadiene, and 50 to 95 isobutylene. The molecular weight can rapidly be brought from 50,000 to 250,000.

When the proportion of butadiene in the reaction mixture is increased, elasticity and pliability are decreased. It is preferred to operate at very low temperature, thus − 95° C. gives better results than − 78° C.

A typical example produced the following results:

	Parts
Isobutylene	120
Butadiene	30
Ethylene (liquid acting as refrigerant and solvent)	300
$Al.Cl_3$–Ethyl chloride (5% in ethyl chloride)	Several

Temperature $-95°$ C.

This gave a white rubber-like material. It was made up into a mixing as follows:

Copolymer	100
Zinc oxide	10
Sulphur	3
Stearic acid	3
Zinc dimethyl dithiocarbamate	1
Mercaptobenzthiazole	0·5
Carbon black	25

Vulcanized for 5 hours at 130° C., it gave a product with good elasticity and fair recovery. It had a tensile strength of 1560 lb. per square inch, and an elongation at break of 1100 per cent. It was very resistant to benzene, ethylene dichloride, and strong acids.

In another patent The Standard Oil Company [21] stated that polymers obtained as described above could be readily separated from unpolymerized material and from diluent-refrigerant materials such as ethylene.

The polymer appears to be a linear-branched chain aliphatic hydrocarbon which is substantially a saturated organic material.

TABLE 197. DEGREE OF SATURATION OF ELASTIC MATERIALS

	Iodine number
Rubber	350
Isobutylene	450
Butadiene	900
Copolymer	6 to 15

The original process for butyl rubber cooled raw materials down to nearly $-100°$ C., obtaining a 20 per cent. conversion to polymer by means of catalyst. The remaining raw materials had to be recirculated. Recent improvements have increased the efficiency threefold.

They further improved their materials by having the diolefinic constituents present in the reaction mixture within certain limits of quantity. The limits vary with different diolefines and conjugated hydrocarbons. For example, isoprene 5 to 0·5 and preferably 1 part may be co-polymerized at a temperature below $-50°$ C. with 95 to

99·5 and preferably 99 parts of isobutylene in the presence of aluminium chloride. Similarly, isobutylene 90 to 99·5 and preferably 98 parts may be co-polymerized at a temperature below − 50° C. with 10 to 0·5 and preferably 2 parts of 2,3-dimethyl-1,3 butadiene in the presence of aluminium chloride. The products obtained are rubber-like and particular vulcanization aids may be used in their vulcanization in addition to sulphur; for example, zinc dimethyl dithiocarbamate or tetra methyl thiuram disulphide.

It is interesting to note that in 1938, the I.G.[10] described rubber-like products obtained by polymerizing isobutylene and butadiene together in the presence of sodium peroxide. The rubbery product could be compounded and vulcanized.

Production of Butyl Rubber. Butyl rubber is produced by an extremely rapid polymerization which is completed in a matter of seconds. The Rubber Reserve SR 43 plant operated by the Humble Oil Co., of Baytown, Houston, Texas, is one of the largest Government-owned synthetic rubber plants producing butyl rubber. It has eight large reacting units and produces 130 to 150 tons of butyl per day. The plant cost approximately 25 million dollars. There is a butyl rubber plant at Sarnia in Canada.

Rapid Polymerization of Butyl. Butyl rubber is a copolymer of isobutylene and approximately 2 per cent. isoprene, the latter introducing sufficient unsaturation to enable the product to be vulcanized. Polymerization occurs with extreme rapidity under the influence of aluminium chloride. To modify the violence of the reaction, to facilitate removal of heat and to secure the product in discrete particles rather than a solid mass the reaction mixture is largely diluted with liquefied methyl chloride.

The cooled mixture of 27 parts of mixed monomers and 73 parts of methyl chloride is introduced to the bottom of a large vertical stainless-steel reaction vessel of about 3500 gallons capacity. The Baytown plant has eight of these reactors of which seven are in actual use with one stand-by. The vessels are jacketed with liquid ethylene as the cooling agent. Each vessel has a concentric cylindrical cooling element of stainless steel containing circulating liquid ethylene inside. The reaction mixture of isobutylene and isoprene is continuously pumped up the middle of this inner cooling element to flow down around it and between it and the outer cooling jacket. Each reaction vessel is insulated with a covering of about 8 in. of cork. The catalyst, a solution of anhydrous aluminium chloride in methyl chloride, is introduced to the reaction vessel at about − 140° F. through three separate nozzles. Immediately the catalyst solution mixes with the monomers a violent

exothermic reaction occurs and the butyl rubber is formed instantaneously.

The mixture of monomers and methyl chloride is cooled to about − 120° F. before introduction to the reaction vessel. It is then cooled to between − 140° and 149° F.; the ethylene jacket being kept between − 145° and 155° F. in temperature.

Recovery of Unreacted Monomers. From the top of the reaction vessel the mixture of polymer, methyl chloride and unreacted monomer passes through a short tube approximately 3 inches in diameter into a thin pipe about 15 inches diameter and 5 feet long, which passes directly into the top of what is known as the flash tank—a vertical cylinder of perhaps 40,000 gallons capacity. As the mixture shoots into the entry tube it is met by steam or hot water. It immediately falls into water at about 150° F. at the bottom of the tank. Unreacted monomers and methyl chloride volatilize. A considerable proportion of the isobutylene does not polymerize. This is recovered, purified and recycled. The small amount of isoprene which does not react is discarded. Zinc stearate (2 per cent. on polymer) and phenyl β-naphthylamine are introduced in the flash tank.

The mixed vapours are pumped off through a condensing system to remove excess moisture and are then compressed, refrigerated and distilled for recovery of the isobutylene and methyl chloride.

Filtering and Drying Plant. As the butyl rubber flows from the bottom of the flash tank it is in the form of white flocks suspended in hot water. This mixture flows to an Oliver filter, where the bulk of the water is separated and the flocks are slightly compressed to a continuous porous band. This is broken into a crumb and conveyed to the drying machine, which comprises several endless belts of perforated steel plate on which the coagulated butyl is taken backwards and forwards along a hot-air oven. In order to prevent the butyl rubber sticking to the conveyor belt, the latter is continuously sprayed with a fine mist of castor oil.

After leaving the drying oven or tunnel the butyl, which has somewhat compacted, is extruded from a 12-inch forcing machine in the form of ribbons about 5 inches wide by ¼ inch thick. Passage through the extruder serves two purposes. It heats the butyl and also dries out a little more moisture. The strips from the extruder pass down to an 84-inch mill, the rolls of which are kept very hot, and here the last of the moisture is dried out and the rubber homogenized. From this mill it is fed to another slightly smaller mill, where it forms a continuous band about ½ inch thick. From this last mill the butyl is cut automatically into individual sheets, which are stacked to form the

TABLE 198. EFFECT OF 30-VOLUME PIGMENT LOAD IN BUTYL RUBBER[a] [7]

Pigment	Tensile strength Lb./sq. in.	Modulus at 400% Lb./sq. in.	Elongation %	Tensile, lb./sq. in., after: 48 hr., air oven, 250° F.	Tensile, lb./sq. in., after: 14 days, o2 bomb
Kosmobile 66 [d]	2690	610	880	1670	1970
Wyex [e]	2560	810	830	1350	1910
Statex	2510	880	670	2660	2560
Cabot No. 9 [e]	2420	640	840	1400	1920
Gastex [f]	2180	660	710	1600	1500
Kosmos 20	2010	850	650	1830	1800
Thermax	1960	445	760	1650	1750
P.33	1880	420	720	1570	1740
Kosmos 40	1810	1330	570	1730	1610
Zinc oxide	2080	60	830	1870	2000
Calcene	1970	60	840	1110	1470
Gilders whiting	1550	120	820	880	1380
Celite No. 270	1350	175	780	715	1070
Silene	1030	200	760	805	1080

Pigment	Tear resistance, Lb./in.	A.S.T.M. permanent set %	Compression set [b] %	Temp. rise [c], ° F.	Shore hardness
Kosmobile 66 [d]	475	34·0	27·7	121	55
Wyex [e]	470	28·0	20·0	111	55
Statex	320	16 0	18·3	63	56
Cabot No. 9 [e]	500	28·5	20·1	112	52
Gastex [f]	225	18·4	20·8	58	46
Kosmos 20	290	16·0	22·9	91	50
Thermax	120	19·9	14·1	54	47
P.33	195	17·2	21·3	59	47
Kosmos 40	365	27·4	22·5	97	59
Zinc oxide	205	22·3	—	—	42
Calcene	155	18·8	29·2	177	37
Gilders whiting	80	22·0	27·1	121	40
Celite No. 270	70	36 6	37·9	146	48
Silene	170	23·1	19·6	161	46

[a] Butyl B, 1·45, 100·0; zinc oxide, 5·0; stearic acid, 3·0; tetramethylthiuram disulphide, 1·0; sulphur, 1·5; pigment, 30 vol. All data on cures of 60 min. at 307° F. except compression set and heat build-up which are 120 min. at 307° F.

[b] Constant deflection.

[c] Measured in Goodrich flexometer.

[d] Representative of the standard rubber channel blacks.

[e] Representative of the easy-processing channel blacks.

[f] Representative of the furnace type blacks.

right weight to fill cardboard boxes. The latter are specially treated on the inside to prevent them sticking.

Processing. The most authentic information about processing of butyl rubber has been given by Haworth and Baldwin.[7]

The actual technique for handling butyl on full-scale factory processing equipment is similar to that for natural rubber with one exception. As a result of an unusually high degree of nerve in the pure gum state, together with a rather low degree of cohesion at elevated temperatures, butyl tends to " lace " and fall from the roll during the early stages of pigment addition when being mixed on a mill. This difficulty may be overcome to a considerable extent by placing a small portion of the batch on a tight cold mill and loading it to a very high degree with the pigment portion of the batch; then the mill may be opened, a normal-sized batch added, and mixing continued in a normal manner. An alternative method is to use a " leader " of a previously mixed batch. The success of these two methods in improving mixing conditions is due to the decrease of nerve and the increase in cohesion at elevated temperature that is brought about by the presence of relatively small amounts of pigments.

Butyl is an ideal material for Banbury mixing since no premastication is necessary before the Banbury operation can be carried out. The condition referred to above which makes for rather difficult handling during the early stages of open mill mixing is not a factor in this operation.

Not only can it be handled in a Banbury mixer, but even in the less robust type of internal mixers used for plastics. The reason is that the material is comparatively plastic to start with, and heat generated in mixing is sufficient to make it process without difficulty. Consequently mastication is unnecessary.

The amount of butyl rubber that can be handled on standard machines is no less than in the case of rubber.

Actually slightly more GR-I can be mixed at one batch, e.g. in a Banbury, than with rubber. Mixing time is relatively short, being of the order of 15 minutes.

Most of the filling materials used with rubber may be employed with butyl rubber. As in the case of other synthetic rubbers, the most important filler is carbon black. Semi-reinforcing types of carbon black appear to be most suitable. For example, loadings up to 100 parts filler to 100 of butyl rubber do not present undue difficulty. High proportions of carbon black may be easily incorporated, and the material holds its physical properties. Butyl rubber is different, inasmuch as reinforcing carbon blacks do not in general increase the tensile strength. The same applies to other inert fillers.

If tensile strength alone is considered, carbon pigments which reinforce natural rubber do not reinforce butyl. However, when the

enhancement of other physical properties, such as modulus and tear resistance, associated with reinforcement are considered, it can be said that the types which reinforce natural rubber also reinforce butyl. The results obtained when the other types of carbon are used in butyl are in line with the general performance of these carbons in rubber compounds.

As to the effect of particle size, over the wide range studied for the thermal and over the narrow range for the channel types the change in this property does not produce any substantial change in physical properties. The reinforcing furnace black shows a decided improvement when particle size is reduced. Further, by the use of this black a higher modulus results than is obtained by using a channel black of about the same particle size. As already indicated, this may be due to the difference in chemical nature of the surface as shown by the difference in *p*H. On the other hand, it may be the result of a difference in the " structure " of the different types.

The hysteresis properties as shown by rebound and heat build-up are influenced by carbon type and concentration in a manner similar to that observed for natural rubber compounds. Although rebound at room temperature is low, an increase in temperature greatly increases it. From this it would be expected that butyl would heat up quickly under flexure but that equilibrium temperature would not be excessive except in severe applications. For a balance of physical properties with low heat build-up, the furnace type carbons are suggested.

The ageing of carbon black compounds of butyl is good. For best ageing, here again the use of the furnace blacks is indicated.

GR-I stocks are very nervy. Pigmentation plus addition of softeners to give soft stocks results in materials that are too soft to retain their shape during cure, an effect which is aggravated by the relatively slow rate of cure.

The use of carbon black does enhance properties other than the tensile strength. It improves abrasion resistance, tear resistance, impact strength and the toughness in a manner comparable to that exerted with natural rubber. Moreover, high loadings do not unduly affect flexing behaviour. Nor do they bring up the hardness beyond a fairly hard rubber, e.g. 70° shore. The tensile strength of products may reach 3600 lb. per square inch, while ultimate elongations can exceed 1000 per cent. This feature has been brought out in a patent of the Standard Oil Development Company.

They described the use of carbon black to strengthen P.I..B copolymer compounds. They suggested the use of 75–200 parts

carbon black per cent. of weight of copolymer. The abrasion resistance is enhanced without affecting the flex resistance.

Example—

Copolymer	100
Carbon black	75
Zinc oxide	5
Stearic acid	3
Sulphur	3
T.M.T.S.	1

Moulded at 155° C. for 120 minutes.
Hard T.S. 2800 lbs. per square inch ; Elongation 1000 per cent.
Flexures, etc., tested on De Matthia machine compared with rubber containing 50 per cent. carbon black.

TABLE 199

	Copolymer + 75% carbon black	Rubber + 50% carbon black
Flexures to initial cracking	1,500,000	140,000
Flexures to complete cracking	5,000,000	850,000
Abrasion loss c.c./H.P. hour	111	210

An investigation on the effects of different types of black fillers carried out by Drogin,[5] illustrated these features.

TABLE 200. COMPOUNDS EMPLOYED [5]

	Pure gum		Reinforcing black		Semi-reinforcing black	
	Rubber	Butyl B	Rubber	Butyl B	Rubber	Butyl B
Elastic material	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	3	3·5	3	2	3
Tuads	—	1	—	1	—	1
Altax	1	—	1	—	0·65	—
Sulphur	2	1·5	2·85	1·5	2·85	1·5
Pine tar	—	—	3	—	—	—
Kosmos 20/Dixie 20	—	—	—	—	60	60
Kosmobile 77/ Dixiedensed 77	—	—	50	50	—	—

Cured to maximum tensile properties at 307° F.

SEMI-REINFORCING BLACK

	Smoked sheet	Butyl B
Plasticity (mm.)	153	220
Extrusion (seconds)	1·2	5·2
Modulus, at 200%	1000	335
Tensile strength (maximum)	2840	1850
Elongation at break	420	660
Shore hardness	65	55
Tear resistance	1165	830
Abrasion resistance	175	218
Percentage Rebound	53	12
Heat build-up, average temp. ° F.	130°	172°
Percentage Compression	4·3	4·2
Percentage Set	4·0	6·0
Shrinkage	4·8	10·6
Electrical resistance	23×10^3	164

REINFORCING BLACK

	Smoked sheet	Butyl B
Plasticity (mm.)	245	265
Extrusion (seconds)	2·2	6·5
Modulus at 300%	1450	450
Tensile strength	4075	2800
Elongation	565	805
Hardness	64	55
Tear	1360	832
Rebound	48	12
Abrasion	202	395
Heat build-up ° F.	137°	207°
Shrinkage	2·9	11·5
Electrical resistance	$7{\cdot}5 \times 10^6$	$3{\cdot}1 \times 10^6$

TABLE 201. COMPARISON OF MIXES CONTAINING CARBON BLACKS [5]

(Properties of rubber rated at 100 in each case)

	Pure gum		Reinforcing black		Semi-reinforcing black	
	Smoked sheet	Butyl B	Smoked sheet	Butyl B	Smoked sheet	Butyl B
Plasticity	100	65	100	58	100	70
Extension	100	—	100	34	100	23
Modulus	100	—	100	31	100	34
Tensile	100	90	100	69	100	65
Elongation	100	98	100	143	100	157
Hardness	100	86	100	86	100	85
Tear	100	17	100	61	100	71
Abrasion	100	—	100	51	100	80
Rebound	100	22	100	25	100	23
Heat build-up %	—	—	—	70	—	42

Softeners may usefully be employed with butyl rubber. They must not be of low iodine number, which eliminate such softeners as pine tar, rosin, factice, and unsaturated fatty acids, all of which have aliphatic unsaturation.

Vulcanization. Vulcanization is dependent to some extent on the degree of unsaturation. This has been shown by experiments carried out on the rate of vulcanization of different butyl rubbers varying in their degree of unsaturation. Normal vulcanizing ingredients are employed with butyl rubber, e.g. sulphur, zinc oxide, etc., in substantially the normal quantities. It should be remembered that a certain amount of sulphur and zinc oxide are already included.

TABLE 202. EFFECT OF TEMPERATURE ON CURING RATE OF BUTYL RUBBER [23]

Cure Min.	138° C (280° F.) Cure		145° C. (293° F) Cure		150° C. (302° F) Cure		155° C. (311° F.) Cure	
	T_B Lbs /sq in	E_B %	T_B Lbs /sq in	E_B %	T_B Lbs /sq in	E_B %	T_B Lbs /sq in	E_B %
15	Undercured		1300	1270	2400	1130	2780	1070
30	1400	1260	1970	1080	3350	1090	3540	1000
60	2720	1180	2640	1000	3360	970	3510	980
120	2930	1030	3360	980	3620	980	3640	970

Accelerators have a profound effect on the vulcanization. The behaviour of accelerators does not parallel what happens with rubber. Certain of the standard types such as tetramethylthiuram disulphide, or this together with mercaptobenzthiazole or zinc dibutyl dithiocarbamate, function just as in the case of rubber stocks. Other common types such as butyraldehyde-aniline, P.P.D. benzthiazyl disulphide, and thiocarbanilide, are quite ineffective. This is bound up to some extent with the extremely low degree of unsaturation of butyl rubber.

A typical mixing consists of:

Butyl rubber	100
Zinc oxide	5
Stearic acid	3
Sulphur	0·5
Tetramethylthiurium disulphide	1

At a temperature of 155° C., the rate of vulcanization of such a mix is comparable with that of a rubber stock being vulcanized with mercaptobenzthiazole. The material is not easily susceptible to overcure.

There is a considerable effort being made to find vulcanizing agents and accelerators which will overcome some of the disadvantages of butyl rubber vulcanizates. These are principally the relatively slow rate of cure and the low modulus, which do limit the applications. Great interest has been roused by the use of materials such as *p*-quinone dioxime together with lead dioxide as activating agents, omitting any addition of sulphur. Quantities of the order of 2 parts quinone dioxime to 6 parts lead dioxide give extremely good results in carbon-black mixes, although the material is very touchy and difficult to process. They also tend to improve the ageing properties. A highly loaded carbon-black mix on this basis will cure in 30 minutes at 140° C.

Vulcanization is achieved by using sulphur and organic accelerators, while there are some special reagents.

Butyl rubber is still regarded as a slow curing material, although recent qualities have shown great improvement in this respect. Determination of the state of cure is a matter of some difficulty. Baldwin, Turner, and Zapp use the optimum modulus as their measure of the state of cure. They considered the action of accelerators in some detail. Their base compound was GR-I 100 parts, zinc oxide 5, stearic acid 3, sulphur 2, semi-reinforcing black 54 and accelerator. The GR-I already contained 1 part zinc stearate and 0·5 parts phenyl-β-naphthylamine.

Accelerator	Parts	Minutes for comparable cure
Tetramethyl thiuram disulphide	1·0	33
Zinc dimethyl dithiocarbamate	1·27	39
Mercaptobenzthiazole	1·5	129
Diphenyl guanidine	0·25	
Benzothiazyl 2-monocyclohexyl sulphenamide	1·5	98

This showed the significance of ultra accelerators. In their view, for the proper balance of cure and for initial physical properties, great care must be taken in the choice of the accelerator-sulphur combinations.

With GR-I zinc oxide is essential to an activator for satisfactory vulcanization.

According to Imperial Chemical Industries Ltd.,[11] the most effective accelerator combination is Vulcafor TMT (tetramethylthiuram disulphide) 1 part and Vulcafor ZDC (zinc dimethyl dithiocarbamate) 1 part per 100 parts GR-I.

They illustrated this with Tables 203 and 204.

TABLE 203

GR-I	100	100
"Kosmobile" 77	50	50
Zinc oxide	5	5
Sulphur	2	2
Vulcafor TMT	1	1
Vulcafor MBT	0·5	—
Vulcafor ZDC	—	1·5

Cure. (Mins. at 153° C.)	30	60	120	15	30	60	120
Tensile strength (kg./cm.²)	161	155	148	160	152	155	148
Elongation % at break	816	669	600	815	640	550	500
Modulus (kg./cm.²) at 300% elongation	32	46	54	30	44	60	68
Modulus (kg./cm.²) at 500% elongation	74	98	120	74	102	136	132
Hardness (B.S.I.)	66	63	63	71	61	57	57
Resilience (%) at 50° C.	32·0	32·5	33·8	28·1	30·5	33·0	35·3
Resilience (%) at 100° C.	45·1	46·3	46·7	42·8	49·4	49·1	48·7

TABLE 204

GR-I . . . . 100 — Zinc oxide . 5 — Vulcafor TMT . 1
"Kosmobile" 77 . 50 — Sulphur . . 2 — Vulcafor ZDC . 1·5

Time of cure (mins.)	Temp. of cure	5	10	15	20	30	60	120	240
Tensile strength (kg./cm.²)	168° C.	150	190	185	182	184	—	—	—
	153° C.	—	190	—	190	172	170	166	—
	141° C.	—	—	—	—	167	168	164	172
Elongation at break (%)	168° C.	920	850	784	718	653	—	—	—
	153° C.	—	870	—	830	715	600	567	—
	141° C.	—	—	—	—	844	695	580	542
Modulus (kg./cm.²) at 300% elongation	168° C.	16	32	37	45	54	—	—	—
	153° C.	—	26	—	36	42	56	58	—
	141° C.	—	—	—	—	28	44	60	76
Modulus (kg./cm.²) at 500% elongation	168° C.	32	69	80	100	123	—	—	—
	153° C.	—	56	—	76	100	130	—	—
	141° C.	—	—	—	—	64	96	132	152
Resilience (%) at 50° C.	168° C.	25·1	29·8	30·7	31·0	32·5	—	—	—
	153° C.	—	28·4	—	30·3	33·3	33·5	34·6	—
	141° C.	—	—	—	—	29·5	32·2	35·0	36·7
Resilience (%) at 100° C.	168° C.	31·2	42·8	44·3	47·5	48·7	—	—	—
	153° C.	—	40·8	—	45·4	48·0	48·3	49·7	—
	141° C.	—	—	—	—	43·1	49·7	53·5	52·2
* Permanent set (%)	168° C.	10·5	—	5·5	—	4·5	—	—	—
	153° C.	—	8·5	—	—	5·0	—	4·0	—
	141° C.	—	—	—	—	7·5	—	4·0	—

* Stretch for 22 hours at 100 per cent. elongation at room temperature; set measured 30 minutes after relaxation of stress.

Using this combination they suggested that minimum vulcanizing times should be:

(*a*) 15 minutes at 168° C. (95 lb./in.^{2} steam)
(*b*) 25 minutes at 153° C. (60 lb./in.^{2} steam)
(*c*) 50 minutes at 141° C. (40 lb./in.^{2} steam).

Quinone dioxime is much too fierce and scorchy for ordinary usage.

The use of quinone dioxime is growing for self-curing cements where 2 parts are generally used.

Among other vulcanizing agents Polyac (made by Du Pont) deserves attention. It is thought to be a dinitrobenzene. It gives a high modulus in carbon black stocks. It tends to be somewhat scorchy but greatly reduces cold flow. It is used for tubing stocks.

The following compound is recommended for the manufacture of GR-I inner tubes: GR-I 100, sulphur 2, fine furnace black 50, lime 3, zinc oxide 5, Thionex 1, Polyac 0·5, paraffin 1, and process oil 5. Physical properties are shown for this stock and comparative stocks. Polyac has the effect in GR-I of stiffening the unvulcanized stock, reducing the tendency of inner tubes to thin out in spots. Thionex used in conjunction with Polyac results in safe processing stocks. The addition of 3 parts of lime to the stock further improves stability at processing temperatures of 250° F. or below and increases activity at normal vulcanizing temperatures.

Ageing Characteristics. Ageing and deterioration of rubber is largely due to the degree of unsaturation. In butyl rubber this is not the case, so that it is intrinsically extremely resistant to ageing, and no antioxidants are necessary.

Long-term ageing tests under conditions of high temperature showed remarkable resistance and maintenance of physical properties. When eventually broken down it only undergoes the softening type of degradation; there is no hardening up. Butyl rubber withstands the effect of oxygen, and it is also almost completely indifferent to attack by ozone. It is affected by sunlight and ultra-violet light, but this is virtually inhibited by addition of a small amount of carbon black.

Butyl rubber possesses a very wide temperature range of elastic properties. Not only is its high temperature behaviour comparable with the elastomers, but in the low temperature range it does not become brittle or lose its rubber-like properties until − 80° F. This is considerably lower than the crack-point of any other elastic material.

Because the original unsaturation is very small, and because even this low unsaturation is greatly reduced (and may even be entirely

eliminated) during the curing operation, vulcanized butyl rubber is extremely resistant to chemical attack. This is true, because it has become, after vulcanization, not only a non-thermoplastic, strong elastic material, but also an essentially chemically saturated product as well. This means that, while from a physical standpoint vulcanized butyl rubber resembles soft vulcanized natural rubber, chemically it may be considered more similar to ebonite.

TABLE 205. EFFECT OF METALLIC SALTS ON DETERIORATION OF BUTYL RUBBER BY OXYGEN.[23]

Metal salt added %	Type of ageing	T_B Lbs./sq. in.		E_B %	
		Original	After ageing	Original	After ageing
—	7 days Geer oven 95° C (203° F.)	2110	1880	1000	1000
1 Cu oleate . . .	Same	2070	2380	1000	1000
0·5 Mn phenol sulphide	Same	2250	2000	950	1020
Same	92 hrs. Bierer bomb, 70° C. (158° F.)	2250	2140	1050	1070

As a result butyl rubber is chemically the most resistant of all elastic materials. It withstands virtually all corrosive influences. Its resistance towards concentrated nitric acid and concentrated sulphuric acid is unequalled. In the same way it is not in the least affected by those metals which have such devastating corrosive influence on rubber. It has been conclusively shown that butyl rubber which has been mixed with copper, manganese, or cobalt salts, has approximately the same tensile strength after ageing as before. Rubber treated in the same manner is completely broken down.

It is apparent that the acceleration of ageing by these metal catalysts is related to the presence of an excessive amount of unsaturation in the rubber molecule.

Tensile Relationships. The stress-strain curve of butyl rubber is different from that of natural rubber. Until an elongation of about 500–700 per cent. is reached the stress is very low, or, put another way, it has a low modulus. This is of great importance because it means that for many purposes the yield of the material under small stresses may be very considerable which is not altogether favourable. Most uses of elastic materials involve precisely these small stresses. From this elongation up to the breaking point, the curve is more nearly like that for

natural rubber. In effect this means that rubber is more rigid than butyl rubber. Also since more energy will be put into rubber for the same deformation, it will obviously retract more energetically. This is shown by the snap of rubber, in contrast to which butyl rubber is rather flabby.

Abrasion resistance of butyl rubber products are quite good, particularly for carbon black stocks. The order of abrasion resistance is illustrated by the fact that butyl rubber employed as the tread on a tyre is said to give between 40 and 50 per cent. of the wear obtained with rubber.

Butyl rubber does not bounce or rebound to any great extent, a property it shares with polyisobutylene. Incorporation of a plasticizer such as *p*-cymene, has a profound effect in increasing this rebound.

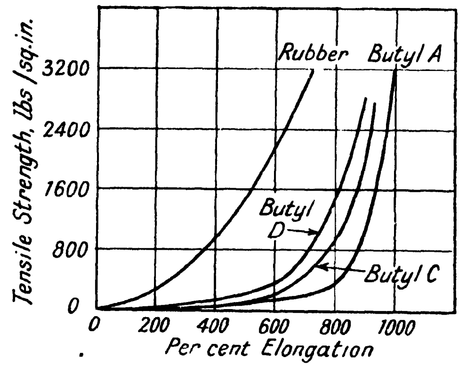


FIG. 89.—Stress–Strain Curves of Butyl Rubbers compared with Natural Rubber.[23]

Yet at 100° C. the bounce is just as good as that of rubber. This shows that butyl rubber has the normal rebound characteristics at a higher temperature range than rubber and that a knowledge of the mechanics of bouncing may enable the shift down to the ordinary temperature range.

Haworth and Baldwin [7] have described how the rebound characteristics may be profoundly improved by addition of small quantities, e.g. 10 volumes, of materials such as benzyl ether, *p*-cymene, chlorinated diphenyl, and trichlorodiphenyl ether. These properties are profoundly affected by the use of quinone accelerators with oxidizing agents such as lead dioxide. Their use improves the modulus, the degree of resilience and lessens hysteresis, without detracting from the tensile strength.

Butyl rubber has excellent flexing and impact characteristics.

Comprehensive tests on the resistance to flex cracking shows conclusively its great superiority over rubber. This superiority is maintained after long periods of ageing during which rubber compounds fail completely. The behaviour is illustrated in Table 125 which records comparative results obtained with comparable tyre tread mixes.

A wide range of products may be produced from butyl rubber compositions. Moulded articles present comparatively little difficulty. Tyre treads have been prepared and have been found to give results about 40 per cent. as effective as with rubber. For the production of calendered articles and frictioned articles the prevailing conditions are much the same as with rubber and must be determined by experiment. Loaded mixes process more easily. Softeners and plasticizers are necessary to facilitate the processing. Somewhat similar conditions apply to the production of tubing and to the covering of wire. In these cases, vulcanization by open steam appears to be most effective.

Calendering Butyl Mixes. The material tends to stick to cold rolls, but comes away readily from hot rolls. It is found that relatively high temperatures are desirable, even up to 200° F. Below 180° F. there are distinct difficulties. Pure gum stocks do not calender satisfactorily, and it is necessary to have more than 20 volumes of filler to obtain good products. Lubricants are desirable to avoid sticking to the middle roll of the calender, and suggested combinations include 3 parts of stearic acid and 3 parts of paraffin wax. It is found that GR-I loaded with carbon black calenders quite readily, whereas the mineral fillers present some difficulties, generally involving more intensive breaking down of the stock prior to calendering. It is an interesting fact that GR-I can give thinner sheets than are obtainable with rubber.

Butyl rubber may be attached to steel. One method uses cements based upon cyclized rubber (e.g. Vulcalock). A film of this is applied to the cleaned steel surface. This is followed by a film of butyl rubber solution heavily loaded with carbon black. The butyl rubber mix is then applied and vulcanization carried through.

Solvent Resistance. Butyl rubber is not primarily a solvent-resisting material. It has, however, a number of interesting characteristic properties. Untreated butyl rubber disperses in benzene, toluene and other aromatic hydrocarbons to give thick viscous solutions. Such solutions are employed for cements, etc. The best solvent is petroleum naphtha. It dissolves in this more readily than rubber does.

GR-I tends to retain its solvents so that the use of solutions, e.g. for spreading, involves longer drying. Generally more coatings are required. Solutions of GR-I have lower viscosities than corresponding

TABLE 206. EFFECT OF TEMPERATURE ON THE FLEX RESISTANCE OF RUBBER AND BUTYL RUBBER.[23]

Flexures	Natural rubber tread	Butyl rubber tread
100° C. (212° F.) tests		
To initial cracking	140,000	Test discontinued after 4,500,000 flexures (no cracking)
To complete cracking	2,800,000	
– 22° C. (– 7·6° F.) test		
To initial cracking	90,000	Test discontinued after 1,000,000 flexures (no cracking)
To complete cracking	260,000	

solutions of rubber. The adhesive properties of GR-I are not as good as in rubber, but are much better than GR-S. Nevertheless, for many purposes the tack available with GR-I is adequate for fabrication. Spreading mixes generally include some wax, e.g. 5 per cent. paraffin wax and up to 50 per cent. fillers.

Although it is swelled by aliphatic hydrocarbon solvents as readily as natural rubber, when vulcanized GR-I has very good resistance to the simple aromatic hydrocarbons, such as benzene and toluene. It is superior to some materials which now are being used for the construction of petrol hose.

It is unaffected by such nitrogen-containing solvents as nitrobenzene and aniline.

Butyl rubber has very good resistance towards vegetable and animal oils, as may be seen from the comparative table.

TABLE 207. EFFECT OF VEGETABLE AND ANIMAL OILS[6]
(Percentage Swelling)

	Natural rubber	Perbunan	Butyl
Linseed oil	124	172	10
Rape-seed oil	106	0·4	6
Soya bean oil	199	0·0	4
Lard	111	0·7	10
Olive oil	121	2·9	12
Oleic acid	196	35·0	10
Cotton-seed oil	84	0·9	10

Butyl rubber is relatively unaffected by some halogenated solvents, such as ethylene dichloride, but may swell more than natural rubber stocks in others.

It is in general unaffected by oxygenated solvents such as ethers, alcohols, and esters.

TABLE 208. ELECTRICAL PROPERTIES MEASURED AT 1000 CYCLES[23]

Dielectric strength (kv./mil.)	Butyl rubber, 0·6		Natural rubber, 0·5	
	Dry	Wet*	Dry	Wet*
Dielectric constant (1000 cycles).	2·11	2·10	2·46	2·76
Power factor, per cent. . . .	0·04	0·05	0·04	0·16

* 88 hours in distilled water; surface wiped dry for measurement.

Butyl rubber products have excellent resistance to moisture. Water absorption of a pure gum butyl rubber stock is only one quarter that of a comparable pure gum rubber stock. This is particularly important in relation to the electrical characteristics which are excellent.

This would be expected from a saturated hydrocarbon free from electrolytes in any form. A comparison between pure gum natural rubber and pure gum butyl rubber also shows that the electrical properties are maintained also after immersion in water.

Gas Permeability. Butyl rubber is much less permeable to gases than is natural rubber, as judged by tests carried out on a variety of gases. In the case of some of these the rate of passage is so low that it has been found difficult to obtain reproducible results.

TABLE 209. APPROXIMATE RELATIVE GAS PERMEABILITIES THROUGH PURE GUM STOCKS

Gas	Ratio of rate of diffusion through natural rubber to rate of diffusion through butyl rubber
Hydrogen	10–12·5
Helium	6 or greater
Nitrogen	10–20
Sulphur dioxide	Very great

Applications of butyl rubber include self-sealing tanks, balloons, boats as floats, gas-masks, inner tubes, mechanical goods, insulation, etc.

Inner Tubes. The normal conditions prevailing for extrusion of rubber articles are generally employed for GR-I mixes. The temperatures and speeds are of the same order. The size of dies is somewhat

smaller to allow for the somewhat greater swelling which occurs when the extruded material emerges.

The outstanding application of GR-I has been in the production of inner tubes. It has been stated that the air-retaining properties of GR-I are such that inner tubes remain inflated over periods of 12 months. In this field of activity the curing combination most favoured has been:

1 part of tetramethyl thiuram monosulphide
0·5 parts of mercaptobenzthiazole
2 parts sulphur

with the addition of 2 parts of stearic acid to aid processing. Vulcanizing times range from between 10 minutes at 320° F. to 16 minutes, depending on the size of the inner tube.

Butyl rubber is already widely employed together with fabric being spread or frictioned. The processing can be carried out without complications and many products are already based on this procedure.

TABLE 210. GR-I—FRICTION STOCK OR SHEETING

GR-I	100	Cure: 20 minutes at 300° F.
S	2	
ZnO	5	
Stearic acid	3	
MBT	1	
TMT	1	
Gastex	35	
Spindle oil	10	

CALENDER CONDITIONS

	Friction temp.	Sheeting
Top	210° F.	200°
Middle	175°	190°
Bottom	200°	180

TABLE 211. GR-I—COVER STOCK FOR HOSE, ETC.

GR-I	100	Cure: 20 minutes at 300° F.
S	2	
ZnO	5	
Stearic acid	3	
MBT	1	
TMT	1	
Gastex	75	
Spindle oil	5	

In the United States proofings are given 90-minute rise to 270° F. and 90 minutes at 270° F.

In proofings the usual fillers are whiting or clay.

TABLE 212. CARCASE STOCKS FROM BUTYL RUBBERS OF INCREASED UNSATURATION [5]

Stock No.	A	B	C	D	E
Formula					
Butyl B—1·45	100·0	—	—	—	—
Butyl B—3·0	—	100·0	100·0	—	—
Butyl B—5·0	—	—	—	100·0	100·0
Zinc oxide	5·0	5·0	5·0	5·0	5·0
Stearic acid	3·0	3·0	3·0	2·0	2·0
Sulphur	1·5	2·0	2·0	2·0	2·0
Gastex	36·0	36·0	36·0	36·0	36·6
Benzyl ether	—	—	10·0	—	10·0
Tetramethylthiuram disulphide	1·0	1·0	1·0	1·0	—
Mercaptobenzothiazole	0·5	0·5	0·5	0·5	1·0
D O T G	—	—	—	—	0·25
Tensile-modulus at 300% elongation					
Cured 15 min. at 307° F.	2000–0–940	2320–210–870	2390–190–860	1370–1310–310	1220–365–640
Cured 30 min. at 307° F.	2540–155–830	2250–460–720	2270–320–760	1180......200	1060–810–360
Cured 60 min. at 307° F.	2540–235–770	1510–685–560	1670–470–570	1070......180	1120–845–360
Cured 120 min. at 307° F.	2480–270–740	1290–730–510	1460–475–560	1150......190	950......260
Rebound, % (cured 60–120 min. at 307° F.).					
Room temp.	28·6–26·1	37·4–38·6	53·9–53·0	42·8–42·4	50·6–51·5
212° F.	51·0–53·0	77·8–80·7	84·9–79·1	67·9–69·0	65·3–71·8
Heat decompn. (cured 60 min. at 307° F.)	Very badly blown	Slightly porous	Slightly porous	Very slight porosity	Slightly porous

The Possibilities of Butyl Rubber for Tyres. Haworth and Baldwin stated that tyres manufactured wholly of butyl B—1·45—gave 20,000 miles' service on passenger cars run at less than 40 miles per hour.

A point of the greatest importance is that two leading companies (U.S. Rubber and Firestone) indicate that, while butyl rubber tyres can be rated as giving only about one-half of the wear of the best natural rubber tyres, and are not capable of standing sustained high speeds, it is nevertheless a fact that tyres suitable for light passenger car service, and giving reasonably good mileages of 10,000 to 12,000 miles, can be made of 100 per cent. butyl rubber, whereas the rubber companies do not yet know how to make the carcase of a tyre from Buna rubber. This means that the tyres for unlimited duty, military service and heavy trucking service, will have to be made of Buna treads and side-walls and natural rubber carcases, mixed with some percentage of reclaimed rubber.

Haworth and Baldwin have examined the possibilities of different grades of butyl rubber for tyre carcases. They considered that there were distinct prospects for "tailor-made" types of butyl rubber.

Reclaimed GR-I. As the volume of GR-I being consumed mounts to large quantities so more and more becomes available for reclaiming. Several satisfactory processes have already emerged. The problem is one of segregation of materials. Quite satisfactory reclaims are obtained which can be used with advantage together with new GR-I compositions.

Busenberg has described some work carried out with such reclaims. His results are shown in the following table.

TABLE 213. BUTYL RECLAIM IN BUTYL INNER TUBE

			Butyl reclaim 1		Butyl reclaim 2	
GR-I	100		80		80	
Reclaim	—		33 4		33·4	
SRF black	50		40		40	
Zinc oxide	5		5		5	
S	2		2		2	
Stearic acid	1		1		1	
TMTD	1		1		1	
Mercaptobenzthiazole	0·5		0·5		0·5	
Bayol RD	3		3		3	
	T_B	E_B	T_B	E_B	T_B	E_B
6 minutes at 307° F.	1410	1000	1380	870	1020	1000
8 ,, ,, ,,	1730	900	1630	800	1630	890
10 ,, ,, ,,	2000	900	1790	790	1700	850
15 ,, ,, ,,	2170	890	1920	740	1920	800
20 ,, ,, ,,	2070	830	2000	750	1990	780

Aqueous Dispersions of Butyl Rubber. The procedure described below is the most satisfactory found to date. The usual dispersing agents for rubber-like substances—soap, glues, gums, clays—are of little use for GR-I. The charge used comprises: GR-I (50 Mooney) 100; chemical plasticizer 0·4; wetting agent 0·5; triethanolamine 3; casein 10; water 114; creaming agent (if desired) 0·2.

The 100 parts of GR-I are mixed with the plasticizer (e.g. R.P.A. No. 3) on a mill at 100° F. for 10–15 minutes. The wetting agent, preferably of the sulphonate type, is then added, the batch is mixed for 5 more minutes and then cooled. At room temperature, the batch is put in an internal mixer or Banbury which is cooled with circulating cold water. After 10 minutes mixing, 23 parts of a casein paste are added, the paste being prepared as follows.

The triethanolamine, 3 parts, are added to 10 parts of water and the solution heated to 150° F. The casein powder, 10 parts, is then sifted into the solution and the whole is mixed to form a stiff paste.

After this paste has been added to the GR-I batch this is mixed for 35–40 minutes, cold, to form a rich dough. Water is then added slowly at about 1 part per 5 minutes, the batch being allowed to take up the water completely before the next addition is made. The amount of water added in each period can be gradually increased as time goes on until 104 parts have been added in a total time of about 2½ hours. At this point the product is a white viscous fluid containing approximately 50 per cent. solids. It can be screened, preserved with a small amount of a phenol or of formaldehyde, and used as such, or it can be creamed to 60–63 per cent. solids by diluting the dispersion to 20 per cent. solids with water, adding 0·2 parts of a suitable creaming agent per 100 solids, stirring the batch for half an hour, and allowing it to cream.

A very interesting product has been obtained from butyl rubbers. They were vulcanized, placed on the mill and mixed with milled natural or synthetic rubber, afterwards vulcanizing the mixture. According to an example, a mixture of isobutylene 70 to 90 parts with butadiene 30 to 10 was polymerized at temperatures ranging from − 50° C. to − 150° C. in the presence of a Friedel-Crafts polymerization catalyst. Polymers of molecular weights 50,000 to 250,000 are obtainable. The following compound was prepared from the copolymer: copolymer 100 parts, sulphur 2, zinc oxide 5, and tetramethylthiuram disulphide 1, to which may be added carbon black 50, stearic acid, and whiting 20. Vulcanization was carried out at 160° C. for 15 to 60 minutes.

The product has the characteristics of a high-grade synthetic rubber,

but can be broken down by re-milling. Other materials which may be mixed with the copolymer are: neoprene, Buna-S, Perbunan, Thiokol, etc. The products of the invention have elongations ranging up to 1100 per cent., tensile strengths up to 3500 lbs. per square inch, high abrasion resistance, high flexing resistance, and high resistance to chemical substances such as acids, alkalis and solvents.

REFERENCES

[1] Baldwin, Turner and Zapp, *Ind. Eng. Chem.*, 1944, **36**, 791.
[2] Brill and Halle, *Naturwissenschaften*, 1938, **26**, 12.
[3] Butlerov and Gorianov, *Ann.*, 1873, **169**, 146.
[4] Dintses and Postnov, U.S.S.R. Patent 59036/1944.
[5] Drogin, *Rubber Age* (N.Y.), 1942, **51**, 483.
[6] Effect of Oils, *Chem. Met. Eng.*, 1942, **49**, 97.
[7] Haworth and Baldwin, *Ind. Eng. Chem.*, 1942, **34**, 1302.
[8] Howard, U.S.P. 2,049,062/1936.
[9] I.G., B.P. 525,542/1940.
[10] I.G., B.P. 490,366/1938.
[11] Imperial Chemical Industries Ltd.—Technical Literature.
[12] Longman, *Rubber Chem. Tech.*, 1941, **14**, 386.
[13] Mann, U.S.P. 2,229,661/1940.
[14] Schwarz, *Kunststoffe*, 1939, **29**, 9.
[15] Sebrell and Dinsmore, *India Rubber World*, 1941, **102**, 36.
[16] Selker, Winspear and Kemp, *Ind. Eng. Chem.*, 1942, **34**, 160.
[17] Shinkle, Brooks and Cady, *Ind. Eng. Chem.*, 1936, **28**, 275.
[18] Sparks, Lightbown, Turner, Frölich and Klebsattel, *Ind. Eng. Chem.*, 1940, **32**, 1283.
[19] Standard Oil Development Co., B.P. 513,521/1939.
[20] Standard Oil Co. of New Jersey, B.P. 560,528/1943.
[21] —— B.P. 523,228/1940,
[22] —— B.P. 540,049/1941.
—— B.P. 537,468/1940, B.P. 537,497/1940, B.P. 539,134/1940, B.P. 565,974/1943.
[23] Standard Oil Development Co. and I.G., B.P. 467,932/1937.
[24] Thomas, Zimmer, Turner, Rosen and Frölich, *Ind. Eng. Chem.*, 1940, **32**, 299.
[25] Thomas, Sparks, Frölich, Otto and Müller-Conradi, *J. Amer. Chem. Soc.*, 1940, **62**, 276.

CHAPTER 19

THIOPLASTS

THE materials dealt with so far have all been based upon butadiene, and have therefore had reasonably close constitutional affinities with natural rubber. There is a very important group of materials outside this. They are formed in the first place by a condensation process rather than one of polymerization.

The thioplasts form an interesting group of synthetic resins based upon ethylene polysulphide. Although they bear no chemical relationship to elastomers yet they have physical rubber-like properties which bring them into the sphere of elastic materials. When the molecular weight becomes high enough, the materials acquire rubbery characteristics. There is some controversy as to whether these should be regarded as synthetic rubbers. Having much in common with many plastics, they occupy a position between thermoplastics and rubber. As synthetic rubbers they are unique in containing sulphur. They have actually been commercially available in the United States in the form of Thiokol since 1931. About the same time a somewhat similar material known as Ethanite was made by the Belgian Cracking Company. Others have appeared on the market since that time, notably the German materials Perduren.

There has been considerable activity with these ethylene polysulphide synthetic rubbers in Germany. For a number of years Thiokols were produced by the Thiokol Actiengesellschaft, and were selling in large quantities. The I.G. were, of course, very interested at a very early stage. They developed the group of materials known as the Perdurens. Until the war these were available in this country. The properties and behaviour of these materials are very similar to those of the various Thiokol types. Similar materials are also made in other countries, in Great Britain, in the U.S.S.R. and in Japan, but on a smaller scale.

At about the same time as Goodyear was working towards his discovery of the vulcanization of rubber, Loewig and Weidmann [10] first isolated ethylene sulphide.

$$\begin{array}{l} CH_2{-}Cl \\ | \\ CH_2{-}Cl \end{array} + K_2S_5 \longrightarrow {-}CH_2{-}CH_2{-}S_5{-} + 2KCl$$

In 1861 Crafts [4] purified this and showed the product to be C_2H_4S.

Meyer [14] in 1887 obtained amorphous ethylene sulphide by boiling ethylene dibromide and potassium sulphide. But since scientists were a long way from recognizing the importance of anything that was not crystalline, nothing further came of any of this early work.

Realization of the possibilities came simultaneously in several quarters. In the early 1920's, Patrick [16] in the United States made the discovery which led to the manufacture of Thiokol, while almost at the same time Baer,[1] at Basle University in Switzerland, prepared a similar material. His work formed the basis on which the I.G. subsequently built their production of Perdurens.

Patrick was fortunate. Seeking a new anti-freeze fluid, he mixed ethylene dichloride and sodium polysulphide, and obtained, not a fluid, but a rubber-like material.

Assiduously following up this discovery, a new industry was started. The first commercially available synthetic rubber to appear on the American market was an ethylene polysulphide polymer designated as Thiokol " A ". This product had many shortcomings: it was not nearly so good as natural rubber at high temperatures, nor was it suitable for use at temperatures below zero Fahrenheit, although at that time this was not a critical factor. Its physical strength was not high; tensile strength of about 900 lbs. per square inch was the maximum. However, it had absolutely unique resistance to all classes of solvents, and it was reasonably cheap. It was furthermore completely unaffected by sunlight, even on several years' exposure, and would withstand ozone without cracking. Finally, its water absorption was only a very small fraction of that of the best rubber compound. Such was " Thiokol " in 1931—several years after Dr. J. C. Patrick had discovered it in a Kansas City laboratory.

The thioplasts were found to have quite remarkable resistance to solvents, oils and greases. Since at that time this filled a demand which could not be satisfied, an important commercial field was immediately available.

As a class these polymers possess excellent ageing characteristics and are relatively inert to a large variety of organic solvents. As to solvent resistance, the materials vary somewhat among themselves. Compounds prepared from the ethylene polysulphide are exceedingly resistant to practically all organic solvents. Those prepared from certain other hydrocarbon polysulphides are resistant to the action of petroleum hydrocarbons, but will swell to varying degrees in certain chlorinated and aromatic hydrocarbons. The behaviour of these polymers in organic solvents is influenced by the groups present in the molecules.

Raw Materials. The ultimate raw materials for the production of these synthetic resins are ethylene (obtained from any of the sources earlier described, but notably from natural gas), sulphur, and salt. They are all relatively cheap. Sodium tetrasulphide is obtained by the interaction of sulphur and caustic soda. Organic dihalides are derived from common organic compounds and chlorine. Chlorine comes from salt, while many of the organic compounds are derived from natural gas, or from acetylene via ethylene. While the United States is undoubtedly most favourably placed for these, yet they are freely available in all industrial countries. This fact, coupled with ease of production, has been regarded as offering an excellent source of synthetic rubber in any national emergency.

By virtue of the suitability of a new type—Thiokol N—for re-capping tyres, really large-scale production in the United States had been carried out. With the arrival of somewhat better materials production has dropped off.

Manufacture of Thiokol. The manufacture of these synthetic elastic materials is simple by comparison with the process required for the other types of elastics.

A simple laboratory method illustrates the ease with which thioplasts may be obtained :

Dissolve 750 gm. sodium sulphide in water and boil with 300 gm. sulphur. This gives a solution containing chiefly sodium tetrasulphide. It is diluted, 500 c.c. ethylene dichloride added, and refluxed at 70° C. for a few hours. At the end of this time a yellow rubbery solid results, which is ethylene polysulphide.

As now produced by the Dow Company,[23] vast storage tanks of sodium polysulphide and of liquid ethylene dichloride stand side by side. Sulphur and sodium sulphide are caused to react in large tanks which form sodium polysulphide. This is filtered and led to the storage tanks. One of the great features of the process is to have a considerable polysulphide supply since large volumes are required. A suitable quantity of sodium polysulphide is pumped into a reactor tank. The requisite quantity of ethylene dichloride is then pumped in and heat is applied with vigorous stirring. After a comparatively short time—a couple of hours or so—a white watery fluid results, which is a synthetic latex. This contains about 80 per cent. water. The Thiokol latex is then successively transferred to other tanks where it is thoroughly washed in order to remove impurities. It is then transferred to coagulating tanks where an acid catalyst is introduced to bring about coagulation. Acid is introduced at a definite rate in order to control the particle size of the product. The coagulated latex is discharged

into a filter where it is washed and excess water is drained off. It is fed between squeeze rolls and then passed on to a continuous dryer, from which it comes off in particle form. It is then finally pressed into blocks ready for transport.

In spite of the ease of production the amount of Thiokol produced has not been as large as might be expected. Authentic figures are somewhat vague. An annual output of about 2000 tons is said to have been reached, although at one time during the war there was very considerable expansion. The limitation has been due to the conservative policy of manufacturing for commercial requirements, which were modest because of the limitations of the materials. For they have some serious disadvantages.

Production in Germany in the past appears to have been on a larger scale. Not only was Thiokol being made and sold under a licensing arrangement with the American concern, but the I.G. were in large-scale production at Saaru. According to one source,[2] production had reached 10,000 tons per annum, i.e. several times the American output. But of course it must be realized that in this case commercial considerations had little to do with output.

Different Types of Thioplasts. By varying the ingredients, notably by substituting other materials for ethylene dichloride, a range of different commercial materials are obtained. Thus Thiokol A is made from ethylene dichloride and sodium polysulphide. It is a greenish-yellow material with a pungent odour and is lachrymatory when heated, e.g. on hot rolls. It contains free sulphur. Thiokol B is made from dichloroethyl ether and sodium polysulphide. It is a more rubbery, darker material than A, with comparatively little odour. It does not give off fumes during mixing. When desulphurized this gave the type known as Thiokol D. Thiokol F (S.G. 1·39) is essentially a disulphide without any free sulphur. It is an amber-coloured rubbery material with comparatively slight odour. A slightly modified Thiokol FA possesses better processing properties, and even less odour than Thiokol F, while not having any material extractable by aviation petrol. This aspect has been more fully discussed by Stevens.[22]

The Perduren series of materials have been developed from somewhat similar materials. According to Stöcklin [23]—

Perduren G is derived from dichloroethyl ether (S.G. 1·68).

Perduren H is obtained from dichloroethyl formal (S.G. 1·56).

Another type is obtained from glycerol dichlorohydrin.

The soft type of material produced in Great Britain, Vulcaplas, is based upon glycerol dichlorohydrin.[8] Another harder white type with comparatively little odour is known as Novoplas A.[14] This is similar to

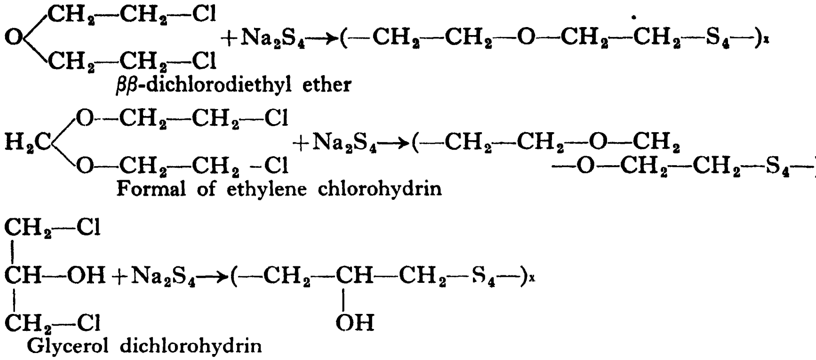


FIG 90.

Perduren G, and intermediate in properties between Thiokol A and Thiokol F, being close to the latter in its processing properties.

The Japanese thioplast known as Thionite is obtained by reacting ethylene diglycoside with sodium tetrasulphide.

Structure of Thioplasts. Patrick[17] has carried out work on the composition of these materials which has brought them into line with other types of plastics. He showed that organic dihalides having a —CH_2Cl group at each terminal, reacted readily with inorganic polysulphides to form long-chain compounds of high molecular weight. When this molecular weight became high enough, rubbery properties were acquired. Molecular growth occurred through elimination of sodium chloride, and in this respect is analogous to the formation of high molecular weight polymers by condensation between dibasic acids and diamines to form long-chain polyamines. So that in effect it is a special case of Carothers condensation. In both cases the reactions involve the interaction of bifunctional molecules to give chain polymers. This reaction can be represented graphically by the empirical equation :

$$XCH_2{-}R{-}CH_2{-}X + MS_XM \longrightarrow$$
$$2MX + {-}CH_2{-}R{-}CH_2{-}S_X$$

Several examples of this reaction are as follows :

TABLE 214

$ClCH_2Cl + NaS_xNa$	$\longrightarrow$	$CH_2S_xCH_2S_xCH_2S_x\ldots$
$ClC_2H_4Cl + NaS_xNa$	$\longrightarrow$	$C_2H_4S_xC_2H_4S_xC_2H_4S_x\ldots$
$ClC_5H_{10}Cl + NaS_xNa$	$\longrightarrow$	$C_5H_{10}S_xC_5H_{10}S_xC_5H_{10}S_x\ldots$
$ClC_2H_4OC_2H_4Cl + NaS_xNa$	$\longrightarrow$	$C_2H_4OC_2H_4S_xC_2H_4OC_2H_4S_x$

This conception would bring Thiokol into line with that other great development—nylon.

Martin and Patrick[12] suggested that the structure of the polysulphide resins is that of long-chain polymers in which the radicals are connected through disulphide linkages and represented as —R.S.S.R.S.S.R—. According to their hypothesis, any additional sulphur in the material in excess of that required to provide the disulphide linkages is believed to be co-ordinately linked to the sulphur comprising the disulphide linkages. The structure is represented as

$$\begin{array}{ccccccccccccc} —R— & S & — & S & —R— & S & — & S & —R— \\ & \| & & \| & & \| & & \| & \\ & S & & S & & S & & S & \end{array}$$

with the added possibility that the co-ordinately linked sulphur may be in a trans- rather than a cis- arrangement. The radical may be derived from ethylene or one of its homologues, or it may be obtained from a reactant containing an ether group, a sulphide group, or an unsaturated group. It is of interest that certain of these products exhibit elasticity both when the amount of sulphur is confined to that representing the disulphide linkages as when the primary molecule contains sulphur in excess of these linkages.

In Thiokol and Perduren two sulphur atoms are part of the main chain while two others are attached to them and are not part of the main chain. According to Patrick, if the latter two sulphur atoms are removed Thiokol A gives an inextensible material. On the other hand, Thiokol B yields an extensible elastic material which has been sold as Thiokol D. This is an amber-coloured material with a very slight odour.

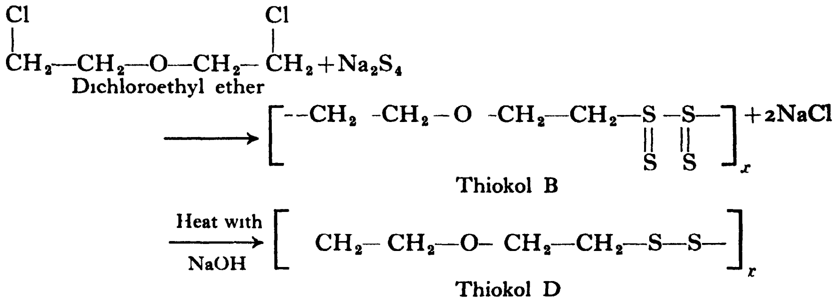


FIG. 91.

The Germans claimed that distinctly improved products were obtained by treating the crude resins with 40 per cent. alkali. According to Spielberger[21] this improved particularly the elasticity and the solvent resistance (as described in an I.G.[9] patent the procedure involved

heating with 40 per cent. caustic soda). Spielberger considered that these thioplasts were made up of "mixed chains" of carbon and sulphur atoms. The great resistance towards solvents was due to sulphur bonds. He thought the vulcanization was caused by a net formation of polysulphide groups.

Commercial Thioplasts. This class of material reaches the consumer in several forms. Most is in the form of sheets and slabs, to conform with normal rubber practice. They are, however, available as suspensions, so that they can be employed in a similar manner to rubber latex. This is a great convenience since thioplasts are so resistant to solvents that the production of solutions is difficult.

Thiokol is also available as moulding powder which greatly increases its scope.

Thioplasts in rubber-like form are handled by the same methods and on the same equipment as are customary for rubber. They are very rubbery, and not particularly thermoplastic, and do not readily form a plastic mass, neither on the mixing mill nor in the Banbury mixer. It is consequently essential to add plasticizers to facilitate the working, the most suitable having been found to be of small amounts of materials such as diphenylguanidine, dibenzthiazyl disulphide, thiuram disulphides, and basic materials generally. Once these have been added, the thioplast works quite easily and the remaining ingredients may be incorporated.

The effectiveness of chemical plasticizers varies with different types of Thiokol. With Thiokol A the most effective are diphenyl guanidine and tetramethyl thiuram disulphide. Diphenylguanidine has the greatest effects, but results in after-hardening, whereas the thiuram is slower working, but does not give after-hardening. For electrical insulation diphenylguanidine is not suitable, and here recourse may be had to thiuram and dibenzthiazyl disulphide.

It is found in the case of Thiokol FA, for example, that the plasticity is controlled by the amount of benzthiazyl disulphide. The softening action exerted is also profoundly accelerated by the presence of 0·2 per cent. of diphenyl guanidine. Depending on the application so the amount of benzthiazyl disulphide is varied, and it is very critical. Thus 0·25 per cent. may give a stiff mix, while at 0·35 per cent. it is likely to be too soft.

The outstanding disadvantages of earlier types of thioplasts, such as Thiokol A, included the dark colour and the pungent odour. In the processing they were distinctly lachrymatory, giving off gas which was most unpleasant. Also when these materials were vulcanized they tended to be porous owing to the trapping of this gas. However, later

materials such as Thiokol F, and FA, are very much better in all these respects, not only the colour and odour being minimized, but there is also a notable decrease of lachrymatory gas. Novoplas A does not smell too badly and is not lachrymatory.

FIG. 92.—Ethylene Dichloride is measured into the Reaction Tank where a Synthetic Latex of Thiokol is formed [24]

It is essential to add carbon black in order to bring out the optimum physical properties. This exerts a definite reinforcing action, the tensile strength being brought up to the highest value obtainable with these materials—1500 lbs. per square inch breaking value, which of course is

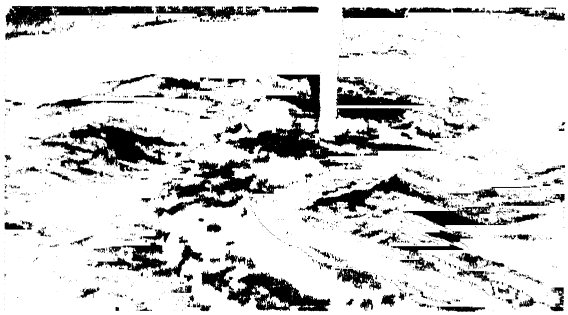


FIG. 93.—Thiokol Latex containing 80% Water and 20% Thioplast.[24]

far less even than an unloaded vulcanized rubber. The best filling materials for Thiokol are semi-hard blacks such as Gastex and soft blacks, notably thermatomic carbon. High proportions of this can be added, up to 200 parts of Thiokol, although a customary loading

is 100 parts to 100. It is usual to add up to 1 per cent. of stearic acid to help the dispersion of these blacks. Although these large quantities of black may be added, exceeding even the amount of thioplast, the effect above 60 per cent. is merely to increase the hardness. Other fillers act merely as diluents and cheapeners, and the usual range applied in rubber manufacture may be used for light-coloured articles. Apart from the use of a little stearic acid as lubricant, other ingredients such as rubber softeners, plasticizers, etc., have little effect, and are not used. Coumarone resins appear to be the most suitable. Materials such as Thiokol are lacking in tackiness, and most softeners do little to augment this.

TABLE 215. TYPICAL THIOKOL A COMPOSITIONS

	Parts by weight		
Thiokol A	100	100	100
Rubber	5	5	5
Diphenyl guanidine	0·25	0·25	0·25
Tetramethyl thiuram disulphide	0·10	0·10	0·10
Zinc oxide	10	10	10
Channel black	10	25	45
Stearic acid	0·5	0·5	0·5
Cured for 50 minutes at 141° C.			
T_B lb. in.^{2}	720	750	950
E_B %	435	305	200
H	64	75	84
% Swelling after 72 hours at 50° C in.			
Petrol	nil	nil	nil
Benzene	4	2·2	1·4

Once compounded, the plastic material formed may be processed in the usual manner, i.e. it may be extruded, calendered, moulded, etc. Those processes involving adhesion present difficulty, owing to the lack of tackiness in Thiokol compounds. Thus impregnation and plying up of these materials are not straightforward processes.

Heat causes materials of this class to vulcanize. In order that the change may come about two things are necessary. There must be a little moisture present, while a certain quantity of zinc oxide is also necessary. Without either of these there is no vulcanization.

According to Patrick[18] the vulcanization that occurs with zinc oxide is an oxidation-condensation with elimination of water, which is thought to explain the change from the plastic to the elastic state.

In the ordinary way about 10 per cent. of zinc oxide is added. With Thiokol A the time required for vulcanization is 60 minutes at 140° C. The change brought about in this way is an improvement in almost every physical property. Tensile strength increases to the maximum

TABLE 216. INFLUENCE OF SEMI-REINFORCING BLACK ON THIOKOL FA [11]

	Part by weight					
Thiokol "FA"	100·00	100·00	100·00	100·00	100·00	100·00
Zinc oxide	10·00	10·00	10·00	10·00	10·00	10·00
Semi-reinforcing carbon black	—	10·00	20·00	40·00	60·00	80·00
Stearic acid	0·50	0·50	0·50	0·50	0·50	0·50
Diphenylguanidine	0·10	0·10	0·10	0·10	0·10	0·10
Benzothiazyl disulphide	0·30	0·30	0·30	0·30	0·30	0·30

Data from sheets cured 40 minutes at 298° F.

Parts black 100 Parts FA	M_{300}	T_B	E_B	Set %	H
0	165	165	310	4	41
10	290	415	430	5	48
20	365	665	520	8	52
40	730	1,200	570	19	63
60	1,110	1,265	420	14	71
80	—	1,375	250	6	80

possible, the modulus and hardness both increase. The tendency for cold flow decreases. The resistance to solvents, oils, etc., is further enhanced.

Actually Thiokol compositions can be cured satisfactorily without any accelerator. 1·5 per cent. of sulphur does, however, help to speed the cure, without introducing risk of scorching.

FIG. 94.—Definite Amount of Acid Catalyst added to give Controlled Coagulation.[24]

One of the most interesting features about compounding these materials, notably Thiokol A, is that in spite of its usual detrimental effect on oil resistance, rubber is one of the most usual additions. It mixes in readily, and facilitates the processing, adds to the tack, and singularly enough does not detract from the oil resistance to any appreciable extent. Additions of the order of 5 to 10 per cent. are usual.

Novoplas A is extensively employed to improve the resistance of Neoprene GN towards oils and solvents. It is also mixed with rubber and elastomers of the buna class. For addition to neoprene and rubber the following procedure is effective.[15]

(1) The Novoplas A is passed through the mill a few times to soften it, roll temperature being 40–50° C.
(2) The nip is closed and masticated rubber is allowed to form a continuous band on the front roll.
(3) The softened Novoplas A is then added in small amounts at a time until all is incorporated into the rubber, the nip being opened as required to give a rolling bank.

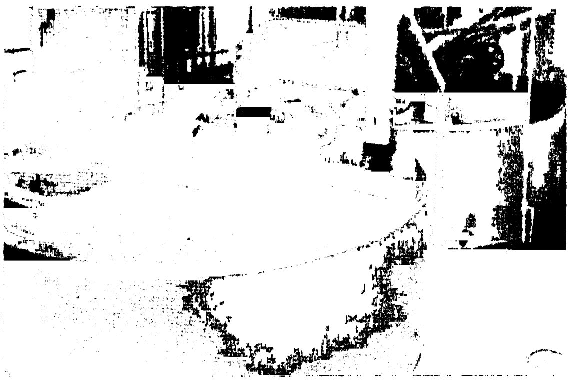


FIG. 95.—Tanks in which Thiokol Particles are thoroughly Washed.[24]

(4) The stearic acid and accelerator are next added and the stock is cut back ten times across the mill.
(5) The carbon black is then added in small quantities at a time, followed by the zinc oxide.
(6) When the fillers are well dispersed, the mix is cut back ten times, then rolled and passed end-wise through a fairly tight nip three times.
(7) After storage, the compounded material should be passed through a mill (roll temperature 40–50° C.) immediately before curing. It is recommended that the material be sheeted to the correct gauge for moulding and that plying up be avoided as far as possible.

Properties of Thioplasts. Thiokol compares favourably with rubber in many of its properties under ordinary conditions, although it is far superior under conditions where oil is present. Its tensile strength

TABLE 217. SOLVENT RESISTANCE OF THIOKOL AT ROOM TEMPERATURE

(Percentage swelling)

Solvent	Thiokol A after 2 years' immersion [a]	Thiokol F after 1 year's immersion [b]	Thiokol FA after 6 months immersion [c]
Motor gasoline	0	1	1·5
80/20 Gasoline-benzol	—	3	3·8
50/50 Gasoline-benzol	—	6·3	8
Benzol	1·5	25	26
Kerosene	0	0·8	—
Motor oil	0	0·5	0
Drip oil	0	13·8	13·8
Linseed oil	—	1·3	0
Cotton-seed oil	—	0	0
Ethyl acetate	—	—	6·3
Duco thinner	0	5	—
Acetone	—	2·5	6·8
Methyl alcohol	—	1·3	4
Carbon tetrachloride	0	8·8	12·3

[a] The Thiokol A mix contained 5 parts natural rubber.[5]
[b] Thiokol F 100 parts; Gastex 60 parts; zinc oxide 8 parts, 60 minutes at 100° C.[5]
[c] Thiokol FA 100 parts; zinc oxide 10 parts; soft black 60 parts. D.P.G. 0·10; benzthiazyl disulphide 0·30 part, 40 minutes at 150°.[11]

does not approach that of rubber compounds, even when reinforced to the maximum, but they retain most of their strength in contact with oils or solvents, these having values which are much higher than those of rubber in the same circumstances. About 1500 lbs. is the top value that can be reached. Thioplasts lack the resilience of rubber at ordinary temperatures. They are much deader. They are little affected by ozone, sunlight, or by oxygen. Although ordinarily the flexing resistance and abrasion resistance are not quite as good as that of rubber or other synthetics, they become far superior in the presence of oils. Under conditions of heat, Thiokol compositions tend to harden up after long periods of exposure. On the other hand, they remain flexible at very low temperatures, Thiokol F, for example, down to $-40°$ F.

The outstanding advantage of these thioplasts is the unequalled resistance to solvents of every kind. They withstand most effectively precisely those solvents which attack other synthetic rubbers. They are incomparable with respect to petrol, kerosene, fuel oils, and lubricating oils. Thioplasts are very resistant to benzene, toluene, xylene, etc., and also to the chlorinated solvents. Right from the time when Thiokol A was first brought on to the market it found wide application for all forms

of hose, dealing with petrol, oils, and solvents generally, and in accessories for industries concerned with these. It is still the leading material for such applications.

Thiokols are unaffected by water, alcohols, and dilute acids. Strong acids such as nitric and concentrated hydrochloric attack them, as do strong alkalis such as sodium hydroxide.

Thiokol Moulding Powders. One type of Thiokol is available as a prevulcanized moulding power which has found a number of important applications.

At present there are several grades of black powder, differing from each other only in physical hardness. The material is a thermoplastic, occupying in its raw state a greater volume than the solid material (3·30 to 1 approx.). It forms at a moulding temperature of about 300° F., under pressure of 700 lbs. per square inch. It has been found that it shrinks in moulding, but that as the shrinkage is always uniform it can be allowed for. The moulding powder is supplied fully compounded and vulcanized. Moulding it is solely a forming operation.

The material may be used in a flash or positive mould with equally good results. It takes about three minutes for the powder to flow and knit together into a smooth, uniformly strong, and highly polished product. More time is needed, however, for pieces larger than 5 or 6 inches in depth and 2 or 3 inches in diameter. Since all trapped air escapes from the material during the moulding operation, it is not necessary to cool the press before opening the mould. Extensive tests on this point have shown that moulded products can be taken from hot moulds without pock-marking or causing porosity. Any flash is reground and used over again.

The most widely used type of Thiokol in the United States at one time was Thiokol DX (which was actually plasticized Thiokol F). It has now been superseded by Thiokol FA. This has extraordinarily good resistance to petrol, oil, and solvents generally. The most effective softener is found to be benzthiazyl disulphide. Very small proportions, less than 0·15 per cent. effectively soften the material on the mill, and greatly facilitate its processing qualities. The vulcanizing agent is zinc oxide, and an addition of between 5 and 10 per cent. is necessary. The setting is accelerated by additions of benzoic acid or sulphur. 0·75 per cent. of benzoic acid reduces the time of cure from 50 minutes to 30 minutes at 50 lbs. per square inch. Further, it increases the tendency for setting up during the processing.

Thioplasts and Cold Flow. As already indicated the great snag which has checked the progress of this class of synthetic rubbers is the

cold flow. Under any degrees of temperature and pressure for any length of time these materials become distorted. Yet under conditions of instantaneous release they are quite as resilient as rubber. The cold

FIG. 96.—Washed Particles are fed into a Filter Box for further Washing, then through Squeeze Rolls on to a Continuous Drier.[24]

flow is of considerable importance, since it means that the products cannot be used under conditions of tension or compression. It also

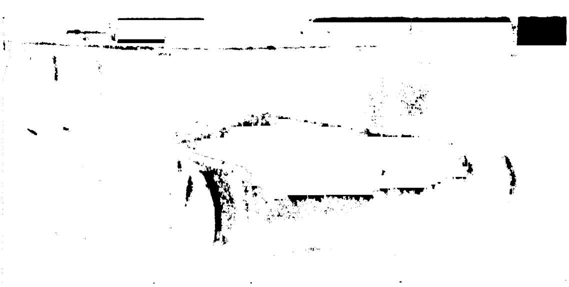


FIG 97.—Dry Thiokol Particles coming off the Continuous Belt being either Pressed into Blocks or Sheeted.[24]

necessitates the cooling of many types of mouldings before extraction, so that there should be no permanent distortion.

The electrical properties are moderate but are comparable with some other synthetic elastic materials. Thus Thiokol A has characteristics

which are not as good as those of raw rubber, but can be compounded to give values comparable with some commercial rubber insulations. According to McPherson,[13] Thiokol A had a dielectric constant of 4–4·5 and a power factor of 0·005 to 0·01, while a compounded sample showed values of 4·5 to 5·5 and 0·015 to 0·035 respectively. Having excellent resistance to ozone, sunlight, oxygen, oils, and corrosive influence, it is extensively employed for cable sheathing, particularly in the United States.

TABLE 218. ELECTRICAL PROPERTIES OF THIOKOL

	Dielectric constant	Power factor	Resistivity ohms/cm.
Raw Thiokol A	4·0–4·5	0·005–0·010	—
Compounded Thiokol A	4·5–5·5	0·015–0·035	$1{\cdot}6 \times 10^{15}$

Impermeability to Gases. These materials are remarkably impermeable not only to solvents but to gases. This is obviously a matter of great importance in these days. Thus Thiokols find wide application for balloon fabrics and other uses where impermeability is undesirable. This property also has some bearing on moulding behaviour since any air that may be trapped cannot get out in the manner in which air gets out of rubber. This shows up as a tendency for porosity to develop.

According to Sagar,[20] films made from this type of synthetic rubber

TABLE 219. PERMEABILITIES TO HYDROGEN OF UNSUPPORTED FILMS

	Average thickness		Permeability		Specific Perme-ability
	cm.	in.	L/sq m / 24 hrs.	Cu. ft./sq. yds/24 hrs.	
Disulphide derivative .	0·030	0·012	0·6	0·018	12·5
	0·025	0·010	0·8	0·024	13·8
	0·017	0·007	1·4	0·041	16·2
	0·015	0·006	1·5	0·044	14·6
	0·011	0·004	2·2	0·065	16·8
Tetrasulphide derivative	0·033	0·013	0·2	0·006	4·5
	0·024	0·010	0·4	0·012	6·6
	0·019	0·008	0·6	0·018	7·9
	0·016	0·006	0·8	0·024	8·8
	0·009	0·004	1·2	0·036	7·5
Rubber	0·030	0·012	10·0	0·295	208
	0·025	0·010	14·2	0·419	246
	0·018	0·007	20·0	0·590	250

are as much as twenty times less permeable to air, hydrogen, and other gases than comparable rubber films ; the same superiority also existed in impregnated fabrics.

The table shows the permeabilities to hydrogen obtained with unsupported films of different thicknesses. The organic polysulphide products represent the disulphide and tetrasulphide derivatives obtained from the reaction between 2,2′-dichloroethyl ether and sodium polysulphide. Values obtained with rubber films of approximately corresponding thicknesses are included for comparison.

TABLE 220. PERMEABILITY OF SYNTHETIC ELASTICS TO HYDROGEN [19]

	Permeabilities to hydrogen at 25° C.
Rubber .	22·8
Perbunan .	14·4
Neoprene G	5·4
Vistanex .	2·6
Thiokol DX.	1·9
Pliofilm .	0·4

Applications of Thioplasts. In spite of the limitations, thioplasts have found extensive use for a wide variety of applications in the United States. The resistance of Thiokol towards petroleum derivatives automatically gives it pride of place in the manufacture of hose of every description for handling petrol and oils. It is used for transferring petrol and oil to and from tankers, for petrol hose, and for the nozzles of such hose. It also features in hose used for paint-spraying, and other uses where solvents are encountered. They are also extensively used for sheathing cables. For similar reasons it is widely used for printers' rollers, for the actual blocks, and for many other printing accessories. From its first appearance the car industry has utilized it for petrol hose, for tank connections, for many types of gaskets, packings and seals. These applications have been a noticeable feature of the United States' activities. Similar activities have occurred in aircraft production, in which another interesting use is in the production of fuel tanks. Resistant beltings and protective clothings are other important outlets. They are in widespread employment for sealing storage tanks of petrol, oils, solvents, etc.

As with the butadiene synthetics, the chief difficulty is due to the lack of tackiness, and chlorinated solvents should be used for swabbing when plying up. Hot splicing has been resorted to in suitable cases, and also the usual methods of treating with natural-rubber cements, but these are limited in their applications and not always very satisfactory. Moulded goods show a marked tendency to porosity due to

the gases evolved during cure, so that it is often advisable to cool off the moulds before breaking and for the same reason hose should be tightly wrapped, using three cross-wraps where two are normally used. Further, the most satisfactory results are obtained with machine-made hose, especially if mechanical aids to adhesion such as open braids and fairly open woven fabrics are employed. Fabrics should be skim coated as well as frictioned, and should be applied with the coat side to the tube. Hoses having natural-rubber covers should have the first ply of fabric frictioned on one side with a Thiokol compound and a rubber friction on the other.

Recent Developments. Apart from the types which have already been mentioned and which are commercially available, there is information concerning new materials in which existing disadvantages have been overcome. For example, one type, Thiokol RD, appears to have comparatively little in common with other Thiokol products, except that it has a very pronounced odour, which is quite different from the characteristic pungent smell. Thus its density of 1·03 is far less than that of any of the other thioplasts. It is much closer in behaviour to the butadiene elastomers and to natural rubber. Thiokol RD is stated to consist of butadiene, acrylonitrile and a third component. Then

TABLE 221. TYPICAL NOVOPLAS A COMPOUNDS [15]

SPREADING MIXES

	Parts	Parts
Novoplas A	90	85
Neoprene GN	10	15
Stearic Acid	1	1
Magnesia	2	3
Mineral Oil	1	1·5
Kosmos 20	30	30
China Clay	—	100
Zinc Oxide	10	10
Vulcafor M.B.T.	0·2	0·2

Cure: 120 minutes at 120° C. in hot air.

EXTRUSION MIX

	Parts
Novoplas A	95
Rubber	5
Zinc Oxide	10
Thermatomic Black	25
Stearic Acid	1
Paraffin Wax	1
Dark Substitute	10
White Substitute	5

Cure: 30 minutes at 60 lb. sq. in. live steam.

nitrogen content is 4 per cent., i.e. one-half that of Perbunan. It behaves rather like Perbunan in many respects. While not possessing quite such good oil- and solvent-resisting properties as the other Thiokol types, yet the mechanical properties are far superior.[6]

Plasticizers and softeners such as are used with neoprene, and with Buna elastomers, are very effective in this instance, for example dibutyl phthalate, tricresyl phosphate, dibutyl sebacate, and the like. Yet on the other hand sulphur and accelerators are used as in rubber compounding, and in similar proportions, while fillers exert comparable reinforcing behaviour. But the most important feature is that cold flow does not occur. For heat resistance sulphur is omitted and a thiuram accelerator is employed.

Processing presents few difficulties. After a few minutes on the mill, which can take almost a full-size batch, all the plasticizers and fillers are added, followed finally by the sulphur. Thereafter calendering, extruding, or any other process may be carried out in the usual manner. Vulcanization requires 50 minutes at 150° C. The tensile strength obtained is of the order of 3000 lbs. per square inch with an elongation of 550 per cent.

There is no tendency for cold flow as exhibited by other thioplasts, the behaviour being nearer to that of the elastomers. Thiokol RD is soluble in acetone and other ketones, in chlorbenzene, ethylene dichloride, etc., and these may be employed for making solutions.

GR-P (Thiokol N). Synthetic rubber, type GR-P, was formerly known as Thiokol N. It is a rubber of the polysulphide class. It was based on the use of propylene dichloride instead of ethylenedichloride. It roused great interest at an early stage in the rubber crisis. It appeared to have great promise and was put forward strongly as a re-treading and re-capping material for tyres. While it performed useful service at a critical period the disadvantages proved rather serious and it faded out. GR-P has been produced from raw materials that were freely available. Manufacturing equipment was relatively simple, and production began fairly rapidly. The material has some disadvantages compared with other Thiokol synthetic rubbers.

The main objective for which GR-P was developed was to substitute for rubber during the period when the main synthetic-rubber programme was building up. It was shown that tyres could be re-treaded with GR-P in commercial retread shops, and that the treads would give reasonably satisfactory service when operated at moderate speeds under average atmospheric conditions.

The great disadvantage of GR-P is the tendency for brittleness and for hardening up as the temperature becomes lower. Stocks based on

GR-P unless modified with reclaim, become brittle at 20° F., while in time they crack at even higher temperatures. Such blends are satisfactory for tread stocks and applications where oil resistance is not too critical a factor.

General Characteristics. GR-P is a light-yellow-coloured solid having a specific gravity of 1·39. It has a characteristic odour and gives off a lachrymatory gas when hot. Unless it is cooled under pressure mouldings tend to be spongy. Because of the gas evolved at elevated temperatures, it is not practical to cure it by festooning in hot-air ovens.

Compounding. A typical formula is GR-P 100; zinc oxide 10; channel black 35; stearic acid 0·5; MBTS 0·4; DPG 0·1.

Zinc oxide is the vulcanizing agent. It is used in amounts of from 5 to 10 parts on the GR-P. Varying the amount of zinc oxide does not vary the rate of cure. Channel black is generally used as a reinforcing filler. It gives best abrasion resistance. The semi-reinforcing blacks are next best, while thermal blacks give the poorest abrasion resistance. Stearic acid is used to aid in filler dispersion, to prevent sticking on mill rolls, calender rolls, and in the mould during curing. MBTS is a chemical plasticizer for GR-P, and the plasticity of the stock is controlled by varying the proportion of this material. For example, increasing the proportion from 0·3 to 0·6 per cent. on the GR-P will change a stiff stock to a very soft one. DPG serves to activate the plasticizing effect of the MBTS. It exerts very little softening by itself. 5 per cent. of diphenyl ether on the batch may be used to plasticize the compound and aid in the incorporation of the black. By its use the mill temperature may be kept down and the tendency to give off lachrymatory fumes decreased.

TABLE 222. TENSILE PROPERTIES OF COMPOUND A

Press cure at 287° F., mins.	M_{300}	M_{500}	T_B	E_B	H
10	185	295	550	1160	54
20	380	595	920	840	60
30	555	850	1110	680	62
40	700	1070	1240	590	63
50	780	1210	1250	520	64
60	815	—	1250	480	65

Bonding GR-P. GR-P compounds tend to be dry and without tackiness. They do not bond readily to themselves when cold, and

this presents a problem in using the material in fabricating parts from calendered sheets.

Ordinary GR-P tends to harden even at room temperatures. This change is comparable to the freezing of crude natural rubber at low temperatures. This freezing does not injure the GR-P, but it does sometimes necessitate thawing it out before mixing.

Compounds mixed from GR-P also tend to harden at room temperatures with age. Such hardened stocks can be thawed at temperatures around 120° F. This hardening of the raw stock is greatly lessened by admixture with reclaimed rubber.

The tendency of cured stocks to harden with age is much less than for uncured material. This tendency is quite pronounced in undercured stocks and less pronounced in the optimum and overcured material.

GR-P has the excellent solvent resistance so characteristic of Thioplasts. This applies to the unblended material. The fact that it has been necessary to mix it with rubber or reclaim to improve its low temperature behaviour greatly limits its application as an oil-resistant rubber.

TABLE 223. PROPERTIES OF THIOKOL RD

Thiokol RD	100
Dibutyl sebacate	20
Zinc oxide	5
Semi-reinforcing black	40
Benzthiazyl disulphide	1
Sulphur	1
Stearic acid	1

Time of Cure Minutes at 298° F.	T_B	E_B	M_{300}	Set %	H
15	2970	580	730	12	52
30	3000	530	1025	12	53
50	3050	530	1070	12	53
90	2640	430	1300	8	54

Swelling after 72 hours at room temperature.

	% Linear swell
Petrol	1
Benzene	29
50/50 Benzene/Petrol	13
Carbon tetrachloride	15

Thioplasts Used with Other Elastic Materials. There are a number of soft thioplasts available, such as Vulcaplas, Thiokol S, etc. While these are often unsuitable for the direct manufacture of articles, yet they are extremely valuable ingredients for admixture with other synthetic elastic materials. For example, in one patent Stöcklin [24] made

TABLE 224. COMPOUNDS EMPLOYED [7]

	Pure gum			Reinforcing black		
	Rubber	Thiokol N	Thiokol RD	Rubber	Thiokol N	Thiokol RD
Elastic	100	100	100	100	100	100
Zinc oxide	5	10	5	5	10	5
Stearic acid	1	0·5	1	3·5	0·5	1
Altax	1	0·35	1	1	0·35	—
D.P.G.	—	0·1	—	—	0·1	—
Sulphur	2	—	1	2·85	—	1
Kosmobile 77/ Dixiedensed 77	—	—	—	50	50	50
Curing temperature	292° F.	287° F.	292° F.	292° F.	287° F.	292° F.

a number of copolymers of butadiene with acrylic nitrile, etc. Although these had very good resistance to oil, he found this was considerably enhanced by the addition of condensation polysulphide thioplasts which were added on the mixing mill. This procedure is now common practice. For example, the excellent oil-resisting characteristics of neoprene are enhanced. Thiokol S is regarded as an excellent plasticizer for Thiokol RD, particularly where the products are to be in contact with solvents, such as petrol, that might extract ordinary plasticizers.

Ordinary types of thioplasts are also finding extensive application to elastomer compositions. In these cases the elastomers confer the desirable high mechanical properties, while the thioplasts confer the

TABLE 225. PROPERTIES OF MIXES WITH REINFORCING BLACK [7]

	Smoked sheet	Thiokol RD	Thiokol N
Plasticity (mm.)	245	457	650
Extrusion (seconds)	2·2	26	36
Modulus at 300%	1450	2200	875
Tensile strength	4075	2925	960
Elongation	565	380	330
Hardness	64	80	70
Tear	1360	385	264
Rebound	48	15	25
Abrasion	202	15	222
Heat build-up (° F.)	137°	184°	187°
Shrinkage	2·9	4·3	0
Electrical resistance	$7{\cdot}5 \times 10^6$	$3{\cdot}4 \times 10^7$	5×10^5

super-solvent resistance. Thus admixtures with Perbunan, Hycar, Neoprene, etc., are widely used.

Thiokol Latex. Thiokol latex is another water dispersion of a rubber-like material which has seen a limited special purpose application. The properties of this latex and its films are considerably different from any described this far. This latex is a stabilized dispersion of polyethylene polysulphide of relatively large particle size (4 to 8 microns). Because of the large particle size coupled with high specific gravity of the polymer (1·5) rapid settling takes place on standing. Concentrates of 65–70 per cent. can be readily obtained by simple settling and decantation of the serum.

This latex can be coagulated with strong acids, but in application usually calls for drying methods only. The outstanding property of Thiokol films is their remarkable resistance to most organic solvents and chemical agents. Because of their low film strength, they do not lend themselves to most latex processes, where this property is important.

The regular sulphur-accelerator type of compounding for rapid cure as used with natural latex and most synthetic latices is not applicable to Thiokol latex. Five to 10 per cent. of zinc oxide is the essential ingredient for cure. Vulcanization accelerators do not aid in cure, but some improve its film-forming properties. Best cures are obtained under pressure, with temperature being reduced before release of the pressure to prevent porosity. Thiokol latex may be compounded with fillers, thickeners, etc., as with natural and other synthetic latices.

Most applications of Thiokol latex are those whereby the compound may be applied by spreading, painting, spraying, or impregnating. This latex is particularly adaptable to tank linings where high solvent resistance is required and odour is no objection.

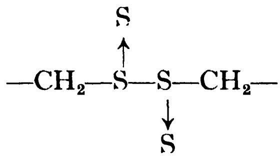
The Detection of Thiokols. The main polysulphate Thiokol types, i.e. tetrasulphide (A, AZ) and disulphide (F, FA), can be easily distinguished in the uncompounded state by the sulphur content but not in the vulcanized state. Parker has described a method which will determine directly which polysulphide type is present even in the presence of natural rubber. Its use for quantitative estimation has been tried, but at the moment a high accuracy is not obtained.

Polysulphide Materials. The structural differences between the two main types of thioplasts are in the amount and mode of combination of the sulphur present. Disulphide materials, such as Thiokols F and FA, contain about 50 per cent. sulphur, the atoms of which are thought to be linked in pairs in the chain of the polymer, whereas tetrasulphide materials, Thiokols A and AZ, contain some 80 per cent. sulphur,

TABLE 226. PROPERTIES OF PURE GUM MIXES [7]

	Smoked sheet	Thiokol RD	Thiokol N
Plasticity (mm.)	121	440	126
Extrusion (seconds)	2·3	90	2·8
Modulus at 300%	210	605	115
Tensile strength	2680	1500	240
Elongation	820	455	700
Hardness	35	50	35
Tear	384	131	41
Rebound	68	—	53
Heat build-up (° F.)	113°	143°	—
Percentage compression	—	3·3	—
Percentage set	4·0	4·0	—

about half of which is attached by co-ordinate co-valencies to the sulphur in the chain, thus:



This co-ordinated sulphur is labile and easily removed by many reagents which are without effect on the sulphur in the polymer chain. In the present instance the reagent used was sodium sulphite, which combines with the sulphur removed, giving sodium thiosulphate which can be estimated by titration.

The method employed is that of Bolotnikov and Gurova [3] for the estimation of free sulphur in rubber vulcanizates. About 0·1 g. of the material is acetone-extracted and then covered with 100 mls. of a 10 per cent. aqueous solution of sodium sulphite. After standing overnight it is boiled for 12 hours and cooled to 0° C.; 10 mls. of 40 per cent. solution of formaldehyde is added, followed by 40 mls. of 20 per cent. acetic acid W/V. The solution is then titrated against standard 0·1 N iodine in the usual way, but in the presence of ice.

If t = mls. of 0·1 N iodine, of factor f, and w = weight of substance taken, the percentage of labile sulphur is $\frac{0{\cdot}321 \times t \times f}{w}$; and if this is all derived from ethylene tetrasulphide the percentage of ethylene tetrasulphide polymer is $\frac{0{\cdot}782 \times t \times f}{w}$.

Table 227 gives the figures obtained on raw uncompounded

polymers, and Table 228 those obtained on vulcanizates of some of these materials.

TABLE 227. TYPES OF THIOKOL AND THEIR SULPHUR CONTENT

Polymer	Total sulphur %	Sulphur in acetone extract	Labile sulphur %	Tetrasulphide calculated from labile sulphur. % calc. in unextracted material
Thiokol A	79·8	11·4	37·9	93·1
,, AZ	84·1	7·3	36·6	89·6
,, F	54·9	0·5	0	0
,, FA	45·1	0·5	0	0
,, N	66·5	3·0	6·2	13·8

TABLE 228. ANALYSIS OF VULCANIZED MATERIALS, BASED ON LABILE SULPHUR

Mix	Polymer	* Theoretical tetrasulphide content, %	Observed tetrasulphide content, %
1	Thiokol AZ	73·5	88·3
2	,, AZ	57·7	65·6
3	,, F	0	0·1
4	,, FA	0	0·2
5	,, FA	0	0
6	,, N	8·7	6·9
7	,, N	8·0	6·4

Assuming polymer contains tetrasulphide as given in Table 227.

Figures of less than about 5 per cent. tetrasulphide content can be ignored (these are obtained from titrations of less than 0·6 mls. of 0·1 N iodine), whilst values above this are a direct indication of the presence and amount of tetrasulphide polymer.

The latest Thiokol—PRI—has greatly improved characteristics, especially at low temperatures, and is about the best oil-resisting material available.

REFERENCES

[1] BAER, B.P. 279,406/1926.

[2] BARKER, *Rubber, History, Production and Manufacture*, U.S. Bureau of Commerce, 1940.

[3] BOLOTNIKOV and GUROVA, *Rubber Chem. Tech.*, 1935, **8**, 87.

[4] CRAFTS, *Ann.*, 1862, **124**, 110.

[5] CRANE, *India Rubber Journal*, 1941, **104**, 30.

[6] CROSBY, *India Rubber World*, 1942, **106**, 133.

[7] DROGIN, *Rubber Age* (N.Y.), 1942, **51**, 483.
[8] GOLDSTEIN, and Imperial Chemical Industries Ltd., B.P. 453,850/1935.
[9] I.G., B.P. 468,369/1937.
[10] LOEWIG and WEIDMAN, *Pogg. Ann.*, 1939, **46**, 81.
[11] MARTIN, *India Rubber World*, 1941, **104**, 30.
[12] MARTIN and PATRICK, *Ind. Eng. Chem.*, 1936, **28**, 1144.
[13] MCPHERSON, *Rubber Chem. Tech.*, 1937, 563.
[14] MEYER, V., *J.C.S.*, 1887, **52**, 228.
[15] Novoplas A., Imperial Chemical Industries Ltd., Technical Literature.
[16] PATRICK, B.P. 302,270/1927.
[17] —— *Ind. Eng. Chem.*, 1936, **28**, 4145.
[18] —— *Trans. Faraday Society*, 1936, **32**, 347.
[19] SAGAR, *Journal of Research of the National Bureau of Standards*, 1940, **25**, 309.
[20] —— *Ind. Eng. Chem.*, 1937, **29**, 747.
[21] SPIELBERGER, *Kautschuk*, 1937, **13**, 137.
[22] STEVENS, W. H., *I.R.I. Trans.*, 1942, **18**, 17.
[23] STÖCKLIN, *Proc. Rubber Tech. Conf.*, 1938, p. 443.
[24] —— G.P. 684,936/1939.
[25] Thiokol Corporation, Technical Literature.

CHAPTER 20

ETHENOID ELASTICS

THE ethenoid resins or vinyl resins are a very important group of materials. They are all based fundamentally upon ethylene, each member possessing the common factor of a vinyl grouping.

The outstanding feature of these materials is that they are thermoplastic, but in many cases they also possess rubbery characteristics. For example, many acrylic esters are intrinsically elastic. In many other cases the elastic properties are dormant, and can be brought into action by the addition of suitable plasticizers or elasticizers. The best example of this is the addition of tricresyl phosphate to polyvinyl chloride. In addition to having rubber-like qualities, they also possess many other useful properties.

The monomeric materials are in most cases liquid, which not only tend to polymerize alone, but will also copolymerize very readily, in many cases with each other. In other cases they will polymerize with materials such as diolefines. Some of these materials have already attained considerable commercial importance, and this is a steadily growing trend. The special characteristics which account for the applicability of these thermoplastics may be summarized as :

(1) Stability to chemicals, more particularly oxidation, ageing, and metallic rubber poisons ;
(2) No taste and odour ;
(3) Good electrical properties ;
(4) High resistance to cold ;
(5) Simple processing properties.

Their mechanical properties in most cases are inferior to those of rubber and elastomer composition.

Among those who have gained importance by virtue of their rubber-like properties the following are outstanding :

Polyvinyl chloride,
Copolymers of polyvinyl acetate,
Polyvinylidene chloride,
Polyvinyl alcohol,
Polyvinyl butyral,
Acrylic esters.

The significance which these materials have acquired is best conveyed by the statistics. Apart from acrylic esters the output of the vinyl materials in the United States at the present time is at the rate of 180 million lb. per year, and still increasing. In Germany in 1944 the capacity was about 30,000 tons per annum. There is large-scale production in Great Britain and in France.

It is interesting to note that styrene, or vinyl benzene is also included in this family of materials, but since its elastic properties are not available in the ordinary working range, this is not considered in detail. Many of these materials are made by emulsion polymerization, and are available as latices. The films deposited from these are distinctly elastic in character.

Polymerization of Vinyl Resins. Vinyl resins in general are prepared by polymerization. The resin molecule consists of a linear chain in which the monomers have reacted with one another at the double bond to form high molecular weight polymers. The reaction may be brought about by irradiation with ultra-violet light or by addition of a small amount of peroxide, ozone, or tetraethyl lead.

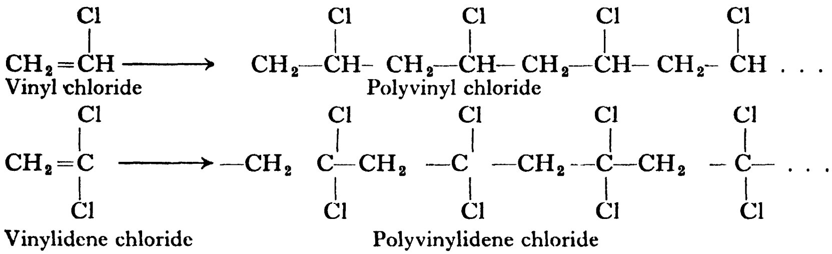


FIG. 98.

Vinyl compound polymerization is a chain reaction in which a large number of molecules react in rapid sequence to form one macromolecule. Polymerization is influenced by several factors. For example, traces of certain impurities act as inhibitors and either retard the rate of polymerization or lower the molecular weight of the resin formed, or both.

According to Douglas,[9] the rate of polymerization varies directly as the square root of the catalyst concentration and doubles with every degree of 8° C. rise in temperature. It is also directly proportional to the concentration of the vinyl compounds present. In other words, solvent lowers the rate of polymerization, and the amount of reduction is specific for each solvent. Average molecular weight, or degree of polymerization of the resin produced, is directly proportional to the solvent concentration in the charge. Compounds that are solvents for

the monomer but not for the polymer affect the molecular weight in the same way as do solvents for the average molecular weight. The latter decreases with increase in temperature and in catalyst concentration. The properties of the resulting resin are closely associated with its molecular weight and with the relative quantities of the various polymer bands of which the resin is composed.

Certain characteristics vary with the average molecular weight, others are independent of it. Thus tensile and impact strengths, abrasion resistance, and viscosity in solution increase, while water absorption, refractive index, hardness, and electrical properties remain practically constant. Solubility in organic solvents rises with decrease in molecular weight.

Historical Background. Not all of these materials are of recent development. Vinyl chloride was obtained as long ago as 1838 by Regnault,[28] who discovered that it could be obtained by the reaction of dichloroethane with an alcohol solution of caustic potash. He discovered that when this was subjected to the action of sunlight in a sealed glass tube, it polymerized to form a white powder. He also discovered vinylidene chloride. Baumann [2] in 1872 succeeded in polymerizing the vinyl halides to white viscous plastic masses which were unaffected by solvents or acids.

The real background to the present importance of polyvinyl chloride was supplied by the work of Ostromislensky,[26] who aptly enough was trying to make synthetic rubber. His work is of outstanding importance. As far back as 1912 he outlined the conditions for the polymerization of vinyl chloride, vinyl bromide, and other derivatives. He also indicated a method for preparing rubber-like materials from the polymerized products. Ostromislensky was particularly interested in seeking a connection between the polymers of vinyl chloride, which he called cauprene chlorides, and chlorinated rubber. He separated fractions from his polymerized vinyl chloride which he called α, β, γ and δ cauprene chlorides.

He actually found that the composition of a vinyl chloride polymer $C_{32}H_{48}Cl_{16}$ was the same as he obtained for a chlorinated synthetic butadiene rubber, and also it was the same as for the chlorinated isoprene synthetic rubber. The similar solubility behaviour of these materials and their common ability to be transformed into plastic masses suggested to him that vinyl chloride was identical with the chlorination products of butadiene, isoprene, and natural rubber. This work first showed the possibility of the industrial utilization of the vinyl chloride polymers. Ostromislensky also developed suitable technique for achieving polymerization.

About the same time Klatte[19] in 1912 had discovered vinyl acetate. This was subsequently found to polymerize without much difficulty. It is the leading starting material for numerous polymers.

The work on acrylic esters and methacrylic esters was for many years carried out by Röhm,[29] whose researches date from 1901.

The use of catalysts such as benzoyl peroxide in order to bring about the polymerization of these materials was described by Klatte and Rollett[20] in 1917.

A considerable amount of work was inaugurated about 1925 in line with the work on other synthetic elastics. Ostromislensky was carrying on his work in this field in the United States. Semon of the Goodrich Company had begun his researches which were to result in the production of Koroseal. There was also a considerable amount of work going on in the same direction in Germany, notably by the I.G. chemists. Under the direction of Pavlovitch these materials have been closely studied and widely utilized in the U.S.S.R.

Herrmann and Haenkel[15] discovered in 1928 that polyvinyl acetate could be hydrolyzed to yield polyvinyl alcohol. Subsequently this was found to have latent elastic properties All this work has led up to the numerous important commercial products, many of which have only been developed during recent years, but which are now firmly established for specific industrial purposes. A notable example, of course, is the use of polyvinyl butyral in the manufacture of safety glass for which it was specially designed.

Polyvinyl Chloride. Polyvinyl chloride is one of the most important commercial synthetic materials which is already produced at a rate of many thousands of tons per year. It is commonly known as PVC. It is widely used in the United States, in Germany, in Great Britain, and in Russia.

In the U.S. in 1943 output was 83 million lb. In 1945 it reached 115 million lb. During 1947 output was 180 million lb.

In the summer of 1944 German production was:

Bitterfield	I.G. Plants	1400 tons per month
Schkopau	I.G. Plants	600 tons per month
Ludwigshafen	I.G. Plants	200 tons per month
Wacker		200 tons per month

giving capacity of 28,000 tons per annum.

British production is of the order of 10 million lb. per annum.

There have been extraordinary developments with polyvinyl chloride as a direct consequence of the shortage of rubber. Wire and cable industries in every country have used the material on a large scale. But intensive development work has widened the scope. Many

diverse fields have opened up, such as waterproof coatings for fabrics, extruded tubing, moulded articles, fabricated sheets, etc.

The outstanding features of the rubber-like masses which can be produced are:

(*a*) Resistance to prolonged flexing.
(*b*) Resistance to sunlight.
(*c*) The materials do not swell in the presence of oils and solvents.
(*d*) Resistance to corrosion.
(*e*) Resistance to moisture.
(*f*) Resistance to oxidation.

Polyvinyl chloride is obtained by the polymerization of vinyl chloride, which is actually a gas at normal temperature, the liquid having a boiling point at − 14° C. Vinyl chloride is obtained chiefly from acetylene, by passing it with hydrogen chloride over a contact catalyst.

There are a number of methods of production of vinyl chloride based on acetylene, dichlorethane, and so on.

Production of Vinyl Chloride from Acetylene. The process of manufacture of vinyl chloride from acetylene actually consists of effecting the union of hydrogen chloride with acetylene in the presence of a catalyst.

The patent literature relating to synthesizing vinyl chloride from acetylene may be summed up in a fundamental formula of passing acetylene and hydrogen chloride, compressing up to 1–1·5 atmospheres, over a contact catalyst. The main points of difference among the many variations of this process is the definition of the temperature range, the selection of catalyst and the plant required for the procedure.

The synthesis of vinyl chloride by this method is carried through according to reaction:

$$CH \equiv CH + HCl \rightarrow CH_2 = C\begin{matrix} \diagup Cl \\ \diagdown H \end{matrix} + 477 \text{ cals.}$$

Vinyl chloride

The temperature level, with liquid catalysts, in the majority of cases is maintained between 60° C. and 80° C. The hydrochloric acid solutions of metal chlorides are the most popular catalysts used in the process.

The following reagents are recommended for application as dry catalysts: (*a*) mercuric chloride precipitated on silica gel; in this case the process of obtaining vinyl chloride may be performed at reduced

temperatures from 20° C. to 30° C.; (*b*) activated carbon, here the reaction is conducted at higher temperature up to 200° C.

The yield of vinyl chloride on the basis of acetylene is usually of the order of 55–70 per cent., and an additional heat economy in the process can be effected by re-circulating exhaust gases.

Judging by the numerous American patent specifications for deriving vinyl chloride from acetylene, it is evident that this method is definitely favoured in the U.S.A.

It is also worth while noting that the rapidly expanding use of the acetylene process for vinyl chloride synthesis in America is paralleled by a similar tendency in Germany. In that country the great reactivity of vinyl chloride, yielding derivatives of far-reaching technical and strategic importance, has been assiduously exploited, and manufacture is carried out on a large scale.

Vinyl chloride is a commodity quite amenable to transportation, and may be conveniently carried in steel bottles or in tank cars.

Apart from the method of production based on acetylene, which has already been described, there are two other methods from dichlorethane which are worth consideration:

First, the manufacture of vinyl chloride by the hydrolysis of dichlorethane. In this process dichlorethane and alcoholic caustic soda are placed in an iron jacketed vessel and dichlorethane is gradually added with continuous stirring. The temperature is regulated by hot water passing through the jacket. The reaction is completed after four hours at a temperature of about 90° C. The procedure is accelerated by increasing the amount of alcohol. The residue left in the vessel at the end of the process may be used over again. The yield of vinyl chloride by this method is between 75 and 85 per cent.

The second method involves the pyrolytic treatment of dichlorethane in the presence of a suitable catalyst. The dichlorethane in the form of gas at high temperature is passed over the catalyst and is cracked. An excellent yield of vinyl chloride is obtained, for example, by passing the vapours over activated carbon between 240° and 350° C. In spite of the advantages this method offers by virtue of the continuity of the process, it is still in the early stages and is being developed.

$$CH_2Cl—CH_2Cl \rightarrow CH_2 \quad CHCl + HCl.$$

Vinyl chloride polymerizes readily by the action of the usual range of catalytic agents. The process may be carried out in solution or under conditions of emulsion polymerization. It is promoted either by light or by heat.

Heat Polymerization of Vinyl Chloride. Under the influence of

heat vinyl chloride readily polymerizes to form resinous substances varying in properties over an extensive range, from rubber-like plastics to hard solids. One method is to add the vinyl chloride together with an acetone solution of the catalyst to alcohol. At 50° C. the reaction may take 80 hours.

Many reagents have been proposed for the use as catalysts in thermo-polymerization of vinyl chloride. It has been suggested, for instance, in Germany to catalyse the reaction with the aid of salts of uranium, cobalt, and lead.[13]

The Carbide and Carbon Chemical Corp.[8] employed tetraethyl lead. Du Pont de Nemours polymerized vinyl chloride by heating it in conjunction with ozonized 90 per cent. methyl alcohol. Lawson [21] recommended the application of small amounts of benzoyl peroxide for polymerization in a chlorbenzol medium conducted in a tin-lined vessel under pressure of 15 atmospheres at 118° C.; the polymer is insoluble in toluol.

Alpha-polymer may be obtained by polymerizing vinyl chloride at 90° C.–120° C. in the following solvents: methyl alcohol, dichloroethane, chlorbenzol, ethyl acetate, benzol, acetone, toluol, in presence of benzoyl or barium peroxides, or ozone, as catalysts.

The polymerization may be accomplished in a solution of methanol, ethanol, pentane, hexane, acetone, aromatic hydrocarbons such as toluol, xylol, in presence of oxidizing catalysts at 40° C.

The polymerization when carried out in alcohol or benzene results in finely dispersed polymeric products.

The German Production of Polyvinyl Chloride (PCU). The polymer formed consists of approximately 700 monomer units.[39]

The chemicals employed are:

(*a*) Vinyl chloride: Pure vinyl chloride made at Schkopau containing no known impurities. Must be free of acetylene and higher chlorinated compounds.
(*b*) Mersolate: The sodium salt of the product formed by reacting SO_2 with a long chain (C_{15} to C_{20}) hydrocarbon made at Leuna.
(*c*) Sodium persulphate: Technical.
(*d*) Hydrogen peroxide: 40 per cent. in water, shipped and stored in carboys.

Description of Process. Two types of polymer are made. One for electrical applications is polymerized with hydrogen peroxide catalyst. The second is polymerized with $Na_2S_2O_8$ catalyst, and is used for all other purposes. Polymerization time is shorter when $Na_2S_2O_8$ is used, and for this reason is preferred when electrical properties are not

important. Two types of drying the polymer are used at Schkopau—spray-drying or coagulating, followed by filtering, washing, compressing, and finally drying with hot air. Two hundred tons per month can be produced by the second method.

Continuous Process. The polymer process is continuous. A more uniform product, having a higher molecular weight and involving simpler plant, are advantages of the continuous process over batch processes.

Each reactor is a jacketed, vertical glass-lined cylinder, 25 feet by 5 feet in diameter, with a paddle agitator in the top seven feet. Ratio of reactants are as follows:

35 per cent. vinyl chloride
3 per cent. mersolate (based on vinyl chloride)
0·5 per cent. hydrogen peroxide or } based on vinyl chloride
0·1 to 0·2 per cent. sodium persulphate } based on vinyl chloride
Balance water

Three streams are metered into the top of the reactor:

(1) The mersolate and water which were previously mixed.
(2) The vinyl chloride.
(3) The catalyst dissolved in a small quantity of water.

Emulsification takes place in the first or upper few feet of the reactor. The temperature is accurately controlled at 45° C. from top to bottom of the reactor by means of a water jacket on the reactor. Reaction time is 3·5 hours with sodium persulphate and 5 hours with hydrogen peroxide. From the bottom of the reactor the emulsion (now 85 per cent. polymerized) is pumped to a helical spiral vacuum evaporator where the excess monomer is flashed off, condensed, and recycled to the polymerizers. The evaporator is about 15 feet high and 8 feet in diameter, jacketed and heat insulated. Exposed parts are of nickel. It is operated at 100 mm. pressure. As the emulsion flows slowly down the spiral path all excess monomer is evaporated without breaking the emulsion. The spiral trough is about 18 to 20 inches wide and 3 to 6 inches deep, and makes one spiral in 12 to 18 inches. One evaporator has capacity for all production to the spray dryer.

The emulsion free of monomer is now either spray-dried or coagulated and dried by conventional methods. When the coagulation method is used aluminium sulphate is added in a glass-lined kettle, the suspension settled, decanted, and filtered on a continuous (Oliver-type) filter approximately 6 feet in diameter with a 3-feet face. The powder is washed on a belt as it passes to a second similar filter. Soda

(0·2 to 0·5 per cent.) is added at this stage as a stabilizer. The damp powder is then compacted on an aeroform continuous press. The resulting pellets are dried at 80° C. on a link screen belt, ground to a fine powder, and packaged in paper bags (50 lb.) for shipment. 0·5 per cent. alphaphenyl indole or 0·5 per cent. diphenyl urea are occasionally used for stabilisers.

Production of PVC by Batch Polymerization. There are a number of interesting features in connection with the batch polymerization of PVC as carried out at Bitterfeld.

Large autoclaves 40 feet long by 3 feet 3 inches internal diameter are used. They are waterjacketed and lined with glass or nickel. The autoclave is charged with an aqueous phase and the vinyl chloride consisting of the following:

(*a*) *Aqueous* phase.

1000 gallons of softened water
400 lb. soap
40 lb. 40 per cent. hydrogen peroxide

These are stirred together until the soap dissolves.

1100 gallons of vinyl chloride

The autoclave is charged and is then rotated, the temperature being brought up to 40° C. by means of warm water in the jacket. It runs in this way for about 24 hours, the temperature and pressure being continuously watched. At the end of the process the pressure drops to ½ atmosphere and the *p*H of the aqueous phase falls from 6·8 to 5. The PVC is then spray-dried and batched.

Properties of Polyvinyl Chloride. Polyvinyl chloride is odourless, tasteless, chemically inert, and non-inflammable except when held in direct contact with flame. It shows thermoplastic properties. It is almost insoluble in all cold solvents, although readily soluble in hot chlorinated hydrocarbons, such as ethylene dichloride or monochlorobenzene. It is soluble in methylcyclohexanone, tetrahydrofurane, mesityl oxide and iso-phorone. Heat and light stability are poor. The high softening temperature of this resin makes milling and moulding difficult because inadequate heat stability prevents the use of temperatures high enough to relieve strains. Tensile and impact strength and other mechanical properties of the pure resin are therefore unsatisfactory. As in the case of other vinyl resins, the average molecular weight of polyvinyl chloride can be varied over a wide range, with corresponding variations in physical properties. According to Buchmann,[7] polyvinyl chloride of low molecular weight, e.g.: 20,000

to 30,000, is unsuitable for plastic purposes but may be used for coating and impregnation. For plastic applications molecular weight must be high, of the order of 60,000 to 130,000. For industrial use polyvinyl chloride is always plasticized.

This is the raw material for the preparation of commercial plastics. Leading products include Vinylite QYNA made by Carbon and Carbide Corporation, Geon made by the Goodrich Co., and Corvic made here by Imperial Chemical Industries Ltd. Geon has molecular weight of 85,000; Corvic has molecular weight of 72,000. It does not find many uses in the straight unplasticized form owing to its comparative lack of flow and the fact that it decomposes very readily at moulding temperatures. The use of straight unplasticized resin has only reached significant proportions in Germany where they found that unplasticized polymer could be extruded, calendered and press laminated. They also made it into drawn film—Luvitherm. The best-known commercial plasticized materials based on straight polyvinyl chloride are Koroseal and Flamenol in the United States. Leading British materials include Welvic made by Imperial Chemical Industries Ltd., Chlorovene made by Cellomold Ltd., and E.25 made by B.X. Plastics Ltd.

TABLE 229. EFFECT OF SIX PLASTICIZERS ON PHYSICAL PROPERTIES OF "KOROSEAL"[32]

Plasticizer	Hardness	Tensile strength		Elongation	Tear resistance	Heat loss	Flexibility limit
		Kg./sq. cm.	Lbs./sq. in.	%	Kg./cm.	%	° C.
A	73	156	2220	350	61·2	2·8	−3
B	76	146	2070	365	63·0	6·3	−1
C	84	160	2280	325	77·6	26·3	+9
D	68	94	1340	380	42·1	32·3	−24
E	69	112	1590	395	42·0	6·6	−22
F	71	112	1590	340	52·3	8·0	−17

Koroseal was developed by Semon,[33] who started work on the problem in 1927, working upon the principles laid down by Ostromislensky. Semon found that polyvinyl chloride was insoluble at ordinary temperatures in practically every known solvent. On the other hand, he found that at high temperatures it was swelled and dissolved by tricresyl phosphate. On the basis of this he was able to develop a method for plasticizing the material with tricresyl phosphate. This can be done by mixing polyvinyl chloride with tricresyl phosphate

at high temperature either in an internal mixer or on open rolls. The essential contents of plasticized material are:

(*a*) Polymer
(*b*) Plasticizers
(*c*) Stabilizer
(*d*) Lubricant

It is necessary to add stabilizers in order to protect the material from decomposition, and in general lead salts are used for this purpose. Typical stabilizers include lead carbonate, lead chromate, litharge, etc., being used in quantities of the order of 5 per cent. of the weight of polymer. Small amounts of lubricant material are added, typical ones being calcium stearate or ethyl palmitate.

When this procedure is carried out, a tough rubber-like elastic mass is obtained, which, however, is thermoplastic, and which can be processed or fabricated by all the methods normally used with rubber. It can be extruded, moulded, or sheeted. Its properties are almost entirely dependent upon the amount and nature of the plasticizer which is added. Among materials employed esters are generally the best, while many ketones and sulphur compounds are satisfactory. The outstanding types of plasticizers for this purpose are tricresyl phosphate, dioctyl phthalate, dibutyl phthalate, diethyl phthalate, etc. Brous and Semon [6] showed how variation in the amount of a single plasticizer gave a remarkably comprehensive range of properties from hard material down to the consistency of the softest of soft vulcanized rubber. Variation between 10 and 60 per cent. of tricresyl phosphate in a polyvinyl chloride mix gave tensile strength varying from 9000 to 1000 lb. per square inch, elongation from 2 to 500 per cent., and hardness from 100 down to 15.

Schoenfeld, Browne, and Brous [32] have shown the different properties obtained for Koroseal prepared with a number of different plasticizers.

Recent technical requirements have made it essential that polyvinyl chloride compositions should retain flexibility at very low temperatures. Plasticizers which achieve this include dioctyl phthalate, dibutyl sebacate, dihexyl phthalate, butyl acetyl ricinoleate, etc. Added in suitable quantities they give compounds which will not crack even at temperatures of 70° C.

Plasticized PVC. Plasticized polyvinyl chloride differs from all the other synthetics discussed so far in one outstanding feature, namely, that it is incapable of being vulcanized. It is a thermoplastic, sensitive to temperature changes, and indeed the only justification for including it with synthetic rubber lies in the fact that the finished product shows

TABLE 230. EFFECT OF AMOUNT OF PLASTICIZER ON PHYSICAL PROPERTIES OF "KOROSEAL" [32]

Vol. Tricresyl phosphate [a]	Hardness [b]	Tensile strength [c]		Elongation [d]	Tear resistance [e]	Oil extract [f]	Gasoline extracts [g]	Heat Loss [h]	Flexibility limit [i]
		Kg./sq. cm.	Lbs./sq. in.	%	Kg./cm.	%	%	%	° C.
50	96	233	3320	190	142·8	0·3	−4·8	1·0	20
75	80	211	3000	270	78·5	2·5	8·8	1·3	7
100	68	147	2100	330	53·6	6·3	15·9	1·3	−5
150	49	98	1400	490	28·6	17·9	19·7	1·4	−22

[a] Per 100 volumes of polyvinyl chloride. [b] Shore Durometer, type A, 30° C.
[c] Force required to break standard dumb-bell at 30° C.
[d] Ultimate elongation at 30° C.
[e] Force (in kg. per cm. thickness) required to tear standard sample at room temperature.
[f] Percentage loss in weight after immersion in oil for 14 days at 50° C.
[g] Percentage loss in weight after immersion in motor gasoline for 14 days at room temperature.
[h] Percentage loss in weight after heating in an air-circulating oven for 14 days at 105° C.
[i] Temperature at which a standard strip under a constant weight will bend through an angle of 30° in 2 minutes.

some similarity to vulcanized rubber, being flexible and possessing some extensibility.

The polymer itself is usually received in the form of a light-coloured powder, capable of aggregating into a hard tough solid. Its molecule is saturated and contains two chlorine atoms for every two carbon atoms, to which may be attributed its toughness. It is converted into a thermoplastic by incorporating tricresyl phosphate as a plasticizer, which causes it to become flexible and capable of being calendered or extruded. That chemical combination between the polymer and plasticizer does not take place is demonstrated by the fact that the plasticizer may be leached out by suitable solvents, and for this reason it undergoes a shrinkage in volume under the action of certain organic liquids. Up to about 50 per cent. of this plasticizer may be incorporated according to the degree of flexibility required, and about 1 per cent. of lead silicate renders the compound transparent. Other lead salts such as litharge are used as stabilizers. Normally, it is a yellowish colour, but by using soluble organic dyes very brilliant and lasting colours may be obtained.

The mixing operation consists of incorporating the requisite amount of plasticizer and colouring matter, and this may be done on the mill in the usual way. If the polyvinyl chloride is soaked in part of the tricresyl phosphate overnight there is less chance of it caking on the

rolls, and a more uniform product is obtained. Only small batches can be handled satisfactorily, the steam should be turned on the mill, otherwise it will be impossible to get the stock to band round the roller. After mixing it should be cut out and hung up in sheets to cool, there being no necessity for dipping or chalking.

Calendering is quite straightforward, the essentials being a very high calender bowl temperature and a steam-heated warming-up mill. The operatives should wear thick gloves, and the feeds should be cut out in strips. Very smooth sheets may be obtained and there is no tendency to stick to the rollers, nor is there any necessity to use liners or glazed holland, as it may be rolled on itself. Besides being calendered into sheets it may be used for frictioning and skim coating fabrics, the usual speeds and friction ratios being suitable.

When handled properly it may be extruded very satisfactorily, but the ordinary extruder as encountered in a rubber works is not well adapted for the best results, as very fine clearances on the worm are required. The worm should be very smooth, in fact it should be highly polished, and it should be steam-heated, as should the barrel, the head, and the warming-up mill. The feeds should be cut out in strips and then laid out on a hot-plate to attain a uniform temperature before being fed into the machine, otherwise variable results will be obtained.

The products do not require any cure, although sheets up to about $\frac{3}{16}$ inch thick are sometimes made by plying up and heating for a short time under high pressure between planished steel plates in a platten press. Splices may be made by pressing joints together and heating, but this is not really satisfactory.

The principal applications are as insulation for wires and for providing acid-resisting joints and packing, as it is extremely resistant to strong oxidizing agents, such as nitric and chromic acids. It can be adapted for tank lining. Methods have been developed whereby it may be bonded directly to steel, wood or concrete.

The material may be further compounded by the addition of a wide variety of filling materials. These tend to make the material shorter and reduce the rubber-like properties. They can confer other advantageous properties such as tensile strength, etc. The quantities used are not very great, up to 25 per cent., for beyond a certain limit the rubber-like properties disappear. The effect of heavy loading is to make the material hard and short; the valuable flexibility at low temperature is adversely affected. Different fillers naturally have different effects. Channel black and silica improve the tensile strength. Softer blacks improve tearing resistance, while other fillers such as clay, whiting, etc., improve oil resistance.

TABLE 231. EFFECT OF HIGH PIGMENT LOADINGS [32]

Polyvinyl chloride	100 vol.
Tricresyl phosphate	89 vol.
Pigment	As specified

Vol. of Pigment	Thermax					Whiting				
	Hardness	Tensile strength		Elongation	Tear resistance	Hardness	Tensile strength		Elongation	Tear resistance
		Kg./sq. cm.	Lbs./sq. in.	%	Kg./cm.		Kg./sq. cm.	Lbs./sq. in.	%	Kg./cm.
0	74	169	2400	335	62·5	74	169	2400	335	62·5
50	84	155	2200	200	94·6	85	122	1730	225	58·9
100	92	169	2410	95	67·9	92	92	1310	120	46·4
150	95	156	2230	45	30·4	95	70	1000	85	26·8
200	96	151	2140	25	8·9	96	67	960	50	19·6

Polyvinyl chloride is not very compatible with many gums, waxes and oils. Compatible materials include chlorinated diphenyls, coumarone resins, rosin, tung oil, coal tar, and asphalt.

The products prepared in this manner have many useful properties. They are elastic, have high tensile strength and elongation, and excellent flex resistance; they are highly resistant to the effect of oils and solvents, they take up only small quantities of water, and they are very resistant to ageing.

At ordinary temperatures the plasticized material will return to its original shape after any distortion up to the breaking point. When distorted, however, it does not snap back to its original shape as does rubber. Its recovery from either elongation or indentation is slow. When slightly distorted, it recovers in a second or so. More severe distortion may require several seconds before recovery, and if it is stretched to a point just below its elastic limit, it may not recover its original size for several minutes. But eventually it always comes back.

These compositions of polyvinyl chloride are unaffected by ozone and oxygen, and by virtue of their chlorine content they do not support combustion. They have some disadvantage, the chief being that they soften at comparatively low temperatures, about 80° C., when plastic flow becomes evident. However, if applied with due appreciation of the temperature limitations, they are excellent materials.

These materials are very inert chemically, and are consequently highly resistant to chemical corrosion. In this connection the nature of the plasticizer must always be considered in case it should be affected by the chemicals concerned. They withstand strong acids such as sulphuric acid, and nitric acid for long periods, and they also withstand

TABLE 232. ACCELERATED AGEING TESTS ON "KOROSEAL"

	Period of ageing	100% modulus		Tensile strength		Elongation
		Kg./sq. cm.	Lbs./sq. in.	Kg./sq. cm.	Lbs./sq. in.	
Bierer bomb	0	98	1390	185	2630	348
	96 hours	105	1490	174	2470	315
	2 weeks	100	1430	172	2440	315
Geer oven .	0	98	1390	185	2630	348
	2 weeks	116	1650	170	2420	275
	2 months	102	1450	174	2470	330

the effect of strong alkalis. For example, they are used for making transparent connections in chemical equipment.

Polyvinyl chloride compositions have excellent resistance towards oils, solvents and greases. They are unaffected by mineral oils, petrol, and so on. The only point about these is the tendency for the extraction of plasticizers, so that in contact with such solvents a suitable plasticizer should be employed. They are not affected by alcohol, glycerine, glycols, etc. They are swelled by chlorinated solvents, by nitro solvents, and by ketones.

While insolubility is an advantage in many applications there is the great disadvantage that it is difficult to stick it. No really satisfactory adhesive has yet been found. The Germans have had some success with polyvinyl ethers such as polyvinyl isobutyl ether.

Polyvinyl chloride is used for flexible tubings and conduits of every description and every degree of flexibility. It is employed to make diaphragms, packings, seals, and gaskets. By virtue of its corrosion resistance it is employed for lining metal tanks. It is used to make transparent tubes for factory and laboratory applications. A notable application is in the brewing industry. It is extensively used for machine parts in the textile industry, where its flexibility coupled with oil resistance make it highly valued.

Polyvinyl chloride compositions are admirably suited for many uses in the cable industry. They have been widely used as a replacement for rubber.

In Great Britain, the cable industry has been the leading user of polyvinyl chloride, and has made numerous important contributions to the technique. Suitably compounded compositions have high dielectric strength, are resistant to ozone, and can be compounded to give lower power factor. The electrical properties have been exhaustively studied.

TABLE 233. ELECTRICAL CHARACTERISTICS

	Polyvinyl chloride	Polyvinyl chloride-acetate	Polyvinylidene chloride
Resistivity (ohms. cm.)	10^{14}	10^{15}	10^{15}
Breakdown voltage (volts per mil.)	750	450	1000
Power factor (60 cycles)	0·1	0·01	0·02
Dielectric constant	6	3·4	4

Barron, Dean, and Scott [1] have described these activities. The use of polyvinyl chloride for every form of wire and cable covering is spreading rapidly. It has a considerable usage for cable covering in the United States, in Britain, in Germany, etc.

Coated wire is fabricated simply by extruding the plasticized material round the wire to the desired dimension. It offers certain advantages over rubber, e.g. no vulcanization process is required. There is a large range of bright colours available, either opaque or transparent. The excellent resistance to solvents and corrosive influences also commend the material for cable application. The material will burn when in a flame but does not otherwise burn; in fact it tends to extinguish flames. Small bores and thin wall thicknesses may be obtained.

Efforts have been made to vulcanize polyvinyl chloride by the use of cross-linking agents, such as allyl succinate.

Electric Characteristics. According to Barron, Dean, and Scott, with the exception of electric strength, the electrical characteristic of polyvinyl chloride are so dependent upon the polymer, plasticizer, extender, filler, etc., employed that a careful check must be made of the compound to determine whether the specified requirements have been met. They showed that the resistivity of compounds which have been plasticised to give $-30°$ C. cold flexibility ranges from 1×10^{10} to 1×10^{12} ohms/cm. cube at 20° C. If less plasticizer is employed (cold flexibility $-25°$ C.), values of 1×10^{12} to 1×10^{14} may be obtained. Further raising of the cold-flexibility temperature coupled with the use of the highest electrical grades of polymer, plasticizer, etc., may enable the resistivity to be raised somewhat above 1×10^{15} at 20° C. This comparatively low maximum value is coupled with a steep resistivity/temperature characteristic which reduces the resistivity to about 1/100th of its value for a rise in temperature of 50° C. It will therefore be realized that polyvinyl chloride insulated cables are not particularly interesting from the insulation-resistance point of view.

Fortunately this characteristic is seldom of real practical value in service. For thermoplastic cables which in service require high insulation resistance a non-polar material such as polythene must be employed.

Similarly, the dielectric loss of the material is high and extremely variable with temperature and frequency. By careful selection of plasticiser and other ingredients, compounds may be produced having reasonable dielectric power factors (e.g. 0·05–0·06). In general, however, such selection imposes serious limitations on the mechanical properties of the compound.

The conclusion must be reached that, except during war emergency, polyvinyl chloride is unlikely to be used as an insulant at frequencies greatly in excess of 2 kc/s.

Similar remarks apply to the permittivity which for an insulating grade at 20° C. works out in general at 6 to 8. Special compounding can achieve values of 4·5 to 6 with the limitations mentioned above. There is also a pronounced temperature coefficient for permittivity.

Extrusion of Polyvinyl Chloride. Polyvinyl chloride is extruded for flexible tubings and conduits of every description and every degree of flexibility. It is employed to make diaphragms, packings, seals, and gaskets. By virtue of its corrosion resistance it is employed for lining metal tanks.

The Germans [38] have carried out extrusion of quite large sections by using piston extruders as distinct from screw extruders. A charge of hot milled compound is loaded in the feed-box and extruded. Tubes up to 12 inch diameter were made in this way.

According to Brous,[5] polyvinyl chloride compositions may be bonded to metals by covering the metal with a coating of chlorinated rubber solution, applying a solution of polyvinyl chloride to this and then attaching the plastic.

Another method uses two adhesives, one for coating the metal—based on polyvinyl acetate, followed by a solution of polyvinyl chloride itself.

It is used to make transparent tubes for factory and laboratory applications. It is extensively used for machine parts in the textile industry, where its flexibility, coupled with oil resistance, make it highly valued.

Calendered PVC. In the form of calendered sheet, polyvinyl chloride is finding wide application. Transparent, translucent and coloured sheets of every description are available. For example, it provides material having suitable characteristics for artificial leather, and a wide field of application is foreshadowed.

Polyvinyl chloride compositions may be calendered in a manner

similar to that used for rubber. The polyvinyl chloride composition is formed into a soft dough on hot mixing rolls. It is then fed on to the calender, which is at a much higher temperature than with rubber. Temperatures are of the order of 125–135° C. Sheetings from 0·015 inches up to 0·125 inches can be made. It is difficult to ply calendered polyvinyl chloride owing to lack of adhesion. Thick sheets of small sizes may be moulded.

Polyvinyl chloride compositions are used for coating cloth. Such fabric is used for raincoats, for shower curtains, and for washable fabrics generally. It is used for upholstery car fabrics, conveyor belts, printing blankets, diaphragms for motors, etc. It can be taken up into solution which is used for coating metals. Another soft form of material can be cast and is used for moulding purposes.

The interesting polyblends obtained from PVC and acrylonitrile rubbers have already been described.

Polyvinyl chloride compositions are widely used for impregnating cloth. Among methods used to coat fabrics is the application of hot pastes of polyvinyl chloride containing plasticizer, and then allowed to cool. MacGill and Morgan have described another method, which is to coat fabrics with homogeneous aqueous dispersions, thereafter removing water, and then causing the particles of plastic to coalesce under heat and pressure. Such fabric is used for raincoats, for shower curtains, and for washable fabrics generally. It is used for car fabrics, conveyor belts, printing blankets, diaphragms for motors, etc.

Polyvinyl chloride can be taken up into solution, e.g. in hot tricresyl phosphate, and such solutions are used for coating metals. Another soft form of material can be cast and is used for moulding purposes.

PVC Pastes. There is a growing interest in the use of PVC in paste form. The paste may be spread on fabric or applied to a mould either by pouring or dipping.

In finely powdered form the polymers are thoroughly mixed with a plasticizing agent in which they are insoluble at ordinary temperatures. No pressure or heat is applied—care must be taken to prevent the mixture being warmed by friction.

According to the nature and proportions of the ingredients, the mixture will be a powder or a stiff, viscous paste which can be further reduced in viscosity by treatment in a roller mill or homogenizing machine. The resultant dispersions may be liquid and mobile, viscous or putty-like. Non-solvent volatile diluents can be used to reduce the viscosity still further.

Gelatinization is effected by heating without the use of pressure. If several coats are applied, each one may be heated for a short time to

ensure adhesion, the whole system being hardened completely after the application of the final coat.

Thus equal parts of polymer and tricresyl phosphate may be used in the following manner:

Mix in an intensive mixer and pass the product through a funnel mill, or alternatively, over friction rollers kept to a temperature below 20° C. a thin lacquer-like paste is obtained, which can be applied with a spray-gun or paint-knife to all sorts of surfaces.

Film formation is effected by heating to at least 160° C., the resultant coating being quite smooth.

Fairweather[11] has described a most interesting application of polyvinyl chloride to modify the properties of other materials, notably neoprene. Neoprene alone slowly absorbs oil, and polyvinyl chloride slowly loses in oils the plasticizers necessary to maintain its flexibility and firmness of shape. It is therefore proposed to obtain better results by using neoprene in conjunction with plasticized polyvinyl chloride. Simple mixing technique consists in plasticizing the vinyl chloride, e.g. with tricresyl phosphate, and adding to the mass a preformed mixture of neoprene and vulcanizing ingredients. A typical composition may be: polyvinyl chloride 100, powdered lead silicate 3½, tricresyl phosphate 75, with 30 parts of neoprene 100, litharge 20, rosin 5, magnesia 3, phenyl beta-naphthylamine 2, maleic acid 2. Such a composition is not appreciably affected by oils over prolonged periods.

According to Brous,[5] polyvinyl chloride compositions may be bonded to metals by covering the metal with a coating of chlorinated rubber solution, applying a solution of polyvinyl chloride to this and then attaching the plastic.

Polyvinyl Chloride in Germany. Polyvinyl chloride has been used on the largest possible scale in Germany.[38] It was used in the plasticized form, in the unplasticized form as paste, and as drawn film.

Plasticized PVC. There is very little difference between plasticized polyvinyl chloride used in Germany and the types used elsewhere. The nature and quantities of plasticizers were also similar. The fields of application include sheetings of all types, supported on fabric and unsupported, floor coverings, cable coverings, extruded products, leather substitutes, and so on. Mipolam was probably as well known a type as any.

Unplasticized Hard PVC. These materials such as Vinidur and hard Mipolam were unique. Straight PVC containing no plasticizer was extruded into tubes and rods, it was calendered, laminated into thick sheets. These materials were brown and translucent. The

materials were strong, light and had outstanding chemical resistance. For this reason they found wide application in chemical equipment.

Comparatively small batches were milled at 160° C., and then calendered at 180° C. Small amounts up to 0·5 per cent. of phenyl indole or diphenyl urea were used as stabilizers.

Tubing of very considerable dimensions were produced, up to 12 inches diameter and ½ inch thick. Extrusion presses were employed, the material being pre-milled at 160° C., and extruded at 200° C. The extrusion method was used to produce pipe, rod, bars, sheet, film and bristles.

These sections were used to make up articles, such as valves, flanged pipes, funnels, developing trays, etc. Hot air welding was used to join parts together.

Polyvinyl Chloride Pastes.[38] Finely ground PVC was dispersed in cold plasticizer and the material could then be handled as a thick paste. This could be poured into moulds, cast on to fabric or cast as sheet. When the temperature of the paste was raised to an appropriate level, the PVC became soluble in the plasticizer, giving a homogeneous rubbery product. The material had high tensile properties and was equivalent to the corresponding product formed by milling. It was used largely for production of shoe soles, for printing rolls, for dipped goods, and for coated fabrics.

Stretched Unplasticized Film (Luvitherm).[38] Rehboch developed this process for unilaterally stretched unplasticized PVC film. A number of machines were making this material.

High viscosity polyvinyl chloride containing 3–5 per cent. of a suitable wax as lubricant and a small amount of stabilizer was ball mixed and then milled at 160° C. For standard production it was carefully calendered to 0·08 mm. It was then passed through a complex system of stretching rolls which reduced the thickness to 0·3 mm. Other thicknesses were also made.

Luvitherm has found wide use for radio recording tapes, electrical tapes, cable wrappings, food packaging, and chemical resistant linings.

Copolymer of Vinyl Chloride and Vinyl Acetate. An important series of resins is obtained by the copolymerization of vinyl acetate and vinyl chloride. They are extremely versatile materials which lend themselves to fabrication by a very wide range of processes. A number of these copolymers have acquired commercial importance. According to the composition, the properties range from those of straight polyvinyl chloride on the one hand, insoluble in solvents, elastic, and difficult to work, to the relatively soluble, more rigid materials with the high proportions of vinyl acetate. Some indications of the versatility is

shown by considering a few applications, which range from gramophone records, flexible tubings and sheetings, to coatings for cans and metals generally.

Efforts were made to use polyvinyl acetate to plasticize polyvinyl chloride, but physical mixtures were in every case found to be unsatisfactory. On the other hand, when the monomeric materials were polymerized together, there was a chemical combination with the formation of a polymer. In this, both vinyl acetate and vinyl chloride formed part of the same molecule chain. The ratio of the two materials can be varied over a wide range. From the point of view of rubber-like properties, these are only apparent when a very high proportion of vinyl chloride is present. In fact the leading product at the present time (Vinylite VYNW) contains 95 per cent. of vinyl chloride, being internally plasticized with the remaining 5 per cent. of acetate. The product has a molecular weight of from 20,000 to 22,000.

According to Benedito,[3] current materials are:

	Vinyl chloride %	Mol. wt.
VYLF	85–88	5,000
VYHH	85–88	10,000
VYNS	88–90·5	18,000
VYNW	95	25,000
VYNU	92–93	
VYNV	98–99	

As the molecular weight and vinyl chloride content rise the resins become less soluble in organic solvents and progressively tougher. When plasticized, they are more elastic and have higher softening temperatures.

As the proportion of vinyl chloride decreases and vinyl acetate increases, so the copolymers formed become increasingly soluble in solvents. Thus materials where the ratio is 90 : 10 readily form solutions and are of interest in the coating field.

The series of resins available has a range of molecular weight from 6,000 up to 25,000. The lower ones at any given temperature are softer and more plastic; the high ones are harder, and have poorer flow.

These copolymer resins are colourless, tasteless, odourless, and non-toxic. They are extraordinarily versatile materials. Their compositions may be used by almost every technique. They are permanently thermoplastic but do not possess a true melting-point, as they merely soften when heated. They will not support combustion. They are produced as a white, fluffy powder, making possible the production of transparent, translucent or opaque articles in the most delicate pastel shades. They are soluble only in ketones and related com-

TABLE 234. PROPERTIES OF TYPICAL COPOLYMER COMPOSITIONS

	Type A	Type B	Type C
Tensile strength, lb. per sq. in.	2500	2000	1300
Elongation, per cent.	300	330	350
Low temperature flexibility, C.	− 17	− 30	− 39
Tear resistance, lb. per in.	30	25	20
Hardness (Shore)	86	75	67
Fatigue resistance, cycles to failure	500,000	> 1,000,000	> 1,000,000
Abrasion loss, vol. in proportion to rubber as 100	80	70	62
Specific gravity	1 23	1·20	1·18

These materials are very resistant to water, soapy water, dilute acids and dilute alkalis, but stiffen when immersed in alcohol, petrol and oil. Other compositions have improved resistance to alcohol, petrol and oil. These are non-inflammable.

pounds, esters, chlorinated hydrocarbons, dioxane, propylene oxide, and mesityl oxide. They swell or dissolve in dichlorethyl ether, and in aromatic hydrocarbons.

They possess extreme chemical inertness, being unaffected by alkalis, oxidizing agents, and most acids. Water, alcohol, and petroleum fractions have no action on them. Thus, in general, they share most of the properties of polyvinyl chloride.

They possess high internal plasticity, permitting the incorporation and use of a large number of different types of fillers and pigments when used in prefabricating operations. They are easier to compound or process than straight polyvinyl chloride. Smaller amounts of plasticizer are required and lower temperatures may be used. Although they darken on prolonged exposure to heat or direct sunlight, these properties may be improved by the use of small amounts, usually 1 or 2 per cent. of stabilizers such as lead stearate, lead oleate, calcium stearate, slaked lime, or somewhat larger proportions of the commonly used lead pigments. These stabilizers should be added to the powdered resin before fluxing on the mill or in an internal mixer. For use where flexibility of the product is a factor, the same range of plasticizers used with the straight polymer are likewise employed. The amount to be used is dependent upon the degree of flexibility required.

General Resistance of Copolymers. Copolymer resins have outstanding resistance towards corrosive agents and solvents. Higher molecular weight resins are in general more resistant, especially to organic solvents, than the lower molecular weight resins. The presence

of other materials such as pigment, wax, stabilizer, etc., in filled compounds or coatings also may alter the behaviour.

The properties of these copolymer plastics vary widely, depending on the grade of resin used, the type and amount of plasticizer, fillers, and other ingredients which may be incorporated. The grade of copolymer will be dependent on the relative proportions of vinyl chloride and vinyl acetate present in the molecule, and the degree of polymerization.

The rubber-like properties are brought out by the addition of plasticizers, similar materials as used with the straight polymer, e.g. tricresyl phosphate, dibutyl phthalate, but a rather wider range is effective in this case than with polyvinyl chloride.

The temperature range in which both polymer and copolymer can be handled is more critical than with rubber compounds, and it must be controlled more accurately throughout the compounding and fabricating processes, as the characteristics and the quality of the final product, as well as its ease of fabrication, are thus influenced.

The actual compounding is done first by blending all of the dry ingredients and preferably the lubricant and plasticizer without heat before feeding to the Banbury mixer. This assures that all of the resin comes in contact with the stabilizer before it is fluxed or heated.

Overheating must be avoided. Mechanical working of large masses generates considerable internal heat, which, if excessive, may bring about undesirable physical and chemical changes in the resin. Even moderate overheating causes a certain loss of plasticity with consequent difficulty in fabricating. Further overheating may cause decomposition with liberation of traces of hydrochloric acid. For the same reason care must be exercised to avoid storing the stock hot for long periods of time.

The same precautions are necessary when transferring the material from the mill to the calender or extruder. Calendering is done with heated rolls with the stock at a temperature of 120° C. to 130° C. The sheeted stock can be cooled either in air or by immersion in water.

The same defects as are found in the polyvinyl chloride, also exist here. The material is rather more heat-stable than polyvinyl chloride, although it is sensitive to traces of iron and zinc which tend to make it decompose.

Elastic Compositions based on Polyvinyl Chloride-Acetate. Plasticized vinyl chloride-acetate copolymer has considerable flexibility, is resilient, and in many respects resembles rubber. Such compositions are resistant to many of those factors which cause rubber to

deteriorate, such as oxygen, ozone, sunlight, in the presence of metallic salts, etc. They have other features such as unlimited colour range and transparency, which are not attainable with rubber. Although they are prepared along similar lines and with similar equipment as used with rubber, yet they do not require to be vulcanized, consequently production is greatly accelerated. Plasticized material is available in a number of forms. Sheets and films are available in all colours, either transparent or opaque, in continuous rolls of varying thicknesses. The materials can be fabricated with everyday equipment. They can be bonded by the use of cements, they can be sealed by heat, or they may be sewn. Other compositions are employed for application to cloth by means of the calender. Other forms are extruded into rods, tubes, and articles of varying cross-sections. The copolymer plastics are extensively used for covering wires and cables.

Apart from these applications they may be moulded either by compression or injection to give a wide variety of products. Among moulded articles of great interest are such things as gramophone records, and tiles. It is advisable to chromium-plate moulds, dies, extruders, etc., or otherwise protect the copolymer from contact with hot iron or steel which attacks it.

Vinyl chloride acetate plastics have excellent resistance to oxygen and ozone. They are unaffected by these agents at ordinary temperatures. They withstand prolonged exposure to sunlight without any marked alteration in physical or electrical characteristics. If properly compounded and plasticized, the materials will not deteriorate over very long periods, even in hot, humid climatic conditions.

The toughness and abrasion resistance are outstanding properties of these materials. The tensile strength is as high as that obtained from high-grade rubber compositions. Specially designed types have abrasion resistance which is superior to that of rubber compounds.

The copolymer plastics are quite non-inflammable and will not support combustion. They are superior to rubber in their ability to withstand the effect of water, oils, and solvents. When properly compounded the materials are also resistant to many acids and alkalis. The elastic behaviour of the flexible materials is impressive. Sheets have been made which could withstand three million flexing cycles under test without cracking. The behaviour under extension is of great interest. Suitable compositions can be stretched to 500 per cent. of the original length. The elastic recovery is much slower than in the case of rubber; it lacks the snap. However, recovery is almost complete and the slow recovery is of use for damping vibration.

While copolymer compositions crack more readily than rubber at

low temperature, suitable compounding enables very low crack points to be attained, e.g. of the order of $-50°$ C.

The electrical characteristics of these materials are quite good, both when wet and dry. They show high dielectric strength at ordinary temperatures of the order of 1000 volts per mil on thin sheets. Di-electric constant at one megacycle per second is of the order of 9 at 70° C.

These plastics can be pigmented to give any colour requirement. Depending on the nature of the pigment they remain stable at exposure to light and to reasonable temperature.

The copolymer has had a very wide application. It can be prepared as a highly polished transparent sheet, glass clear, or in any colour. It is used for many articles of attire such as belts, garters, and suspenders, shoe fabrics, raincoats, and so on. It has also been fabricated into such things as umbrellas, handbags, tobacco pouches, trunks, flooring, and numerous other diverse articles. It is employed for the coating of fabrics and so on. Artificial leather is made by applying tough flexible composition of vinyl chloride-acetate copolymer on to a sturdy fabric backing by means of a calender. Thereafter it can be embossed or given any desired surface grain effect, etc. Such products are likely to have a big future for upholstery. One outstanding use in the United States has been the coating of binoculars.

Applications. Cloth is coated with these plastics on a very large scale. Thinner coatings than with rubber are found to give satisfactory service, so that light-weight proofings are extensively made. Raincoats, tarpaulins, and floating equipment are outstanding examples of current applications.

By comparison with rubber these coatings do not tend to become sticky in hot climatic conditions. They are moisture-proof; and they are free from odour under all conditions.

Cloth coated with heavy coatings of these elastic materials are used for heavy service, such as upholstery applications in aircraft, tanks, and ships. They are found to have all the necessary characteristics for hard usage.

The plasticized copolymers are widely used for covering wires and cables. In this respect the copolymers share the field with straight polyvinyl chloride plastics. They have the advantage over rubber of being non-inflammable, resistant to abrasion, and resistant to corrosion.

Extruded tubing is also exclusively used for hose of various descriptions to handle water, oil, petrol, etc. There are many other applications in the extruded form.

Moulding Technique. These materials are well suited for mould-

ing, either by compression or by injection. For compression-moulding steel moulds, or preferably chromium-plated moulds may be employed. Pressures range from $\frac{1}{2}$ ton to 1 ton per square inch. Temperatures range from 110° C. up to 170° C. depending on the composition. All articles must be cooled under pressure before removal. This affords a very useful method for making flexible articles. Compression-moulded articles include gas-mask parts and accumulator components. A whole range of small articles are made by injection moulding for use in many forms of water equipment.

In the extruded form the use for covering wires and cables takes pride of place. It is also extruded as tubings of every type.

The Production of Vinyon Thread. It is utilized as thread in fabrics (e.g. *Vinyon*), for industrial purposes and as tape and strip for a variety of uses. The type of copolymer used for these applications is made up of 89 per cent. vinyl chloride, and 11 per cent. vinyl acetate.

This degree of copolymerization is interesting in that the vinyl acetate seems adequately to plasticize the vinyl chloride internally, and no other plasticizer is necessary.

The copolymer resin, as a white fluffy powder, is dissolved in acetone to get a rather heavy, viscous spinning dope containing about 25 per cent. by weight of the resin in solution. This is filtered, de-aerated, and spun downwards in air through multiholed stainless-steel jets, just as is done in acetate spinning, the solvent acetone being removed by a current of warm air and recovered. After being conditioned on the take-up bobbin the yarn is stretched either directly or after being plied with one or more ends. The method resembles that used for making cellulose acetate yarn, etc. They have the appearance of long transparent skeins like knitting yarn. The yarn is set by heating, while under tension, to about 90–100° C. This treatment makes the yarn stable to shrinkage up to at least 65° C., but when heated above this temperature shrinkage of the yarn occurs with a corresponding reduction in tenacity and increase in elongation. Mineral acids do not attack "Vinyon" at room temperature, even in high concentrations; it is also unaffected by water; in fact, it may be considered water-repellent, although its surface can be wetted by using some of the commercial wetting agents. Small amounts of "Vinyon" staple have been successfully used in making cotton, wool, and glass felts; the thermoplastic resin functions as a binder, which not only gives added strength, but shortens the time of manufacture. Its largest use at the present time is in the manufacture of industrial filter cloth, because of its unusual properties. Other suggested uses are for shower curtains, bathing suits, waterproof acid and alkali-resisting

clothing, fully-fashioned hosiery, fireproof awnings, etc. Material having a diameter of 0·07 mm. has been used for hat trimmings and synthetic jewellery, etc. These yarns can be braided, knitted, or crocheted.

Copolymers of Vinyl Chloride. The leading German copolymers were the Igelits.[41] Their compositions were as follows:

TABLE 235

	Igelit MP-A	Igelit MP-AK	Igelit MP-K
Vinyl chloride	80	80	86
Methyl acrylate	20	10	14
Isobutyl maleate	—	10	—
Applications	Transparent materials, dials, instruments.	Moulding powder for battery boxes.	Cable insulation.
Output	80 tons per month	20 tons per month	100 tons per month

Igelite MP-A was known as Astralon and was widely used wherever transparent material was required.

Vinylidene Chloride. In effect vinyl chloride is an ethylene molecule containing a single chlorine atom. It is possible to introduce another chlorine atom attached to the same carbon, in which case vinylidene chloride is formed. This is a colourless liquid boiling at 31·7° C.

Vinylidene chloride may be polymerized much along the same lines already described for vinyl chloride. The actual polymer is a white powder, which has no taste, no odour, is non-toxic and does not burn. In actual practice, vinylidene chloride is generally copolymerized, for example with vinyl chloride. In this manner a range of materials becomes available, ranging from the resins which are flexible, and for which there are some solvents, and which soften at about 70° C., up to hard, tough, thermoplastic, for which there are no solvents, and with a high softening point exceeding 180° C.

These materials have even better resistance to corrosion than has polyvinyl chloride. They have virtually no water absorption, and are practically unaffected by most acids and alkalis in all concentrations. They present certain difficulties in processing owing to the high temperatures that have to be used. It is also necessary to have special equipment owing to the fact that iron tends to decompose the material at processing temperatures. The outstanding commercial product is known as Saran, manufactured by the Dow Chemical Company.

Up to the present time the most spectacular application has been in

TABLE 236. RANGE OF PHYSICAL PROPERTIES OF SARAN RESINS[36]

Specific gravity		1·6–1·75
Refractive index	n_d	1·60–1·63
Tensile strength	lbs. per inch²	Up to 60,000
Elongation	%	25
Modulus of elasticity	lbs. per inch² × 10⁵	0·4 × 2·4
Flexural strength	lbs. per inch²	15,000–17,000
Thermal conductivity	10⁴ cal. per sec. per sq. cm./° C. per cm.	2·2
Specific heat cal. per	° C. per gm.	0·32
Resistance to heat	° F. (continuous)	160°–200°
Softening point	° F.	200°–325°
Distortion under heat	° F	150°–200°
Tendency to cold flow		Slight
Volume resistivity	ohm-cms. (50% relative humidity and 25° C.)	6 × 10¹³
Breakdown voltage	60 cycles volts/mil (instantaneous)	500–2500
Dielectric constant	60 cycles	3·0–5·0
" "	10³ cycles	3·0–5·0
" "	10⁶ cycles	3·0–5·0
Power factor	60 cycles	0·03–0·08
" "	10³ cycles	0·03–0·15
" "	10⁶ cycles	0·03–0·05
Water absorption	Immersion—24 hrs.	0·00
Burning rate		None
Effect of age		Becomes stronger
" " weak acids		None
" " strong acids		None
" " weak alkalies		None
" " sunlight		Slight
" " organic solvents		Highly resistant
" " strong alkalies		None
" on metal inserts		Inert
Clarity		Transparent to opaque
Colour possibilities		Unlimited

the form of extruded fibres which have been drawn. This procedure enables the production of materials with extraordinary high tensile strength, and with outstanding ability to resist flexing. These materials are being widely used for woven and braided articles. Filaments of the material are being widely applied for the production of textiles, fabrics, fishing lines, and a variety of similar purposes calling for great strength or corrosion resistance. Apart from this, the material is extruded as rod or tubes, or any desired cross section in continuous lengths.

One outstanding application for the material is as transparent tubing for use in chemical industries for the transfer of corrosive liquids. The material is also moulded, either in the ordinary way or by injection, to give a wide range of products. Vinylidene chloride polymers have

fairly good electrical characteristics which seem to offer prospects of wide application. The leading vinylidene chloride copolymer is with vinyl chloride, the best known being Geon 200.

Polyvinyl Alcohol. The monomeric material vinyl alcohol has so far not been isolated. It is, of course, isomeric with ethylene oxide. Nevertheless, the polymer of polyvinyl alcohol is a material of some commercial importance. It is obtained by the hydrolysis of polyvinyl acetate. This was first carried out by Herrmann and Haenkel,[15] who found that they could hydrolyze polyvinyl acetate by means of both acid and alkali.

TABLE 237. PHYSICAL PROPERTIES OF RESISTOFLEX

	Extruded	Moulded
T lb.in.^{2}	5236	2121
E %	213	445
Permanent set %	78	80
Cold flow %	63·2	63·6
Dielectric strength volts per mil	6·1	10·7
Resistivity ohm cm.	$3{\cdot}1 \times 10^7$	$3{\cdot}8 \times 10^7$

In the United States polyvinyl alcohol is the basis of synthetic elastic material known as Resistoflex. It is made by Du Pont de Nemours. The raw materials are available as white powders which are odourless, tasteless, and soluble in water.

For commercial use they are best made as copolymers with a small proportion of polyvinyl acetate. They can be made resistant to water by treatment with various reagents, such as formaldehyde, chromium compounds, dibasic acids, or copper ammonium compounds. They can be plasticized and then moulded or extruded under moderate conditions of temperature and pressure to give rubber-like articles, or tubes, or coatings. A wide variety of products are now made, including sheets, gloves, gaskets, diaphragms, washers, and tubings.

The outstanding feature of polyvinyl alcohol is the ability to withstand oils, fats, and most organic solvents, including chlorinated hydrocarbons, carbon disulphide, alcohols, esters, ethers, ketones, etc. In fact it is the only flexible material that is completely unaffected by petrol, oils, and most solvents. It is extremely resistant to the action of oxygen and ozone. For example, when subjected to the oxygen bomb test at 300 lbs. pressure of oxygen at 160° F. for ten days it was virtually unchanged. It seems to be almost immune to ageing. Polyvinyl alcohol has high tensile strength and withstands vibration and flexing. Tubing made from it has the singular property of transmitting sound with a minimum distortion and there is no sound absorption by the walls of the tube.

TABLE 238. EFFECT OF SOLVENTS

Tensile strength after 240 hours' immersion at room temperature.

	Lb./sq. in.
Original	5236
Petrol (with lead)	5255
Kerosene	5247
Benzene	5290
Xylene	5351
Acetylene	5340
Trichloroethylene	5140
Carbon tetrachloride	5084
Ethyl alcohol	5779
Ethylene glycol	4335
Acetone	5203
Ether	4980
Butane gas	5332

Polyvinyl alcohol has even better resistance to abrasion than has rubber. It is also only one-twentieth as permeable to gases and liquids.

Polyvinyl Acetals. Polyvinyl alcohol behaves chemically very much like other alcohols, and can be made to undergo a variety of chemical reactions. An outstanding example is the reaction it undergoes with aldehydes when subjected to heat in the presence of a suitable catalyst. Thus in the presence of sulphuric or hydrochloric acid typical acetals are formed. Thus with acetaldehyde, polyvinyl acetal is formed ; with formaldehyde polyvinyl formal, and with butyraldehyde polyvinyl butyral is formed.

The method of manufacture of polyvinyl acetal is essentially to polymerize vinyl acetate, hydrolyse the polymer to polyvinyl alcohol, and react the polyvinyl alcohol with an aldehyde to form an acetal. The properties of the resulting resin depend on several factors. They include the viscosity of the original polyvinyl acetate which indicates the chain length of the molecule, the degree of completion of both the hydrolysis and acetalization, and the nature of particular aldehyde used in the acetal reaction.

The viscosity of the polymer is generally made as high as commercially possible because greater toughness at elevated temperatures results. Where the resin is to be used in solution, lower viscosity polymers are made. This enables thinner solutions to be made with higher solid contents.

In any vinyl acetal the hydrolysis reaction is never complete. Some acetate groups always remain in the polymer chain. It is also customary to acetalize only a portion of the polyvinyl alcohol so that generally several hydroxyl groups are also on the chain. Since the remainder of the molecule is acetal, it is evident that any vinyl acetal can be widely

varied, depending on the quantity of the three groups present on the one molecular chain—hydroxyl, acetate, or acetal.

Finally, the longer the molecule used to form the acetal, the more easily is the resin plasticized. This fits in with the accepted spacer effect of side groups. For example, if formaldehyde is used, the resin requires almost equal quantities of a liquid plasticizer to form a plastic material. If octyl aldehyde is employed, the resin itself is fairly flexible with no plasticizer added at all.

In actual practice the process is carried out direct from polyvinyl acetate, since the hydrolysis, too, may be carried out in the presence of acid. The resin is finally recovered as a white precipitated powder which can be stabilized, purified, and dried.

The following method describes how they may be made:[4]

One hundred parts of polyvinyl acetate is dissolved in 185 parts of glacial acetic acid. To this is added 83 parts of formalin and a suitable amount of a mineral acid, e.g. 6·8 parts of concentrated sulphuric acid. This is hydrolysed in an enamelled vessel at 70° C. Samples removed from time to time are analysed for the formalin content, which indicate how far the acetate has been converted to formal. When the desired

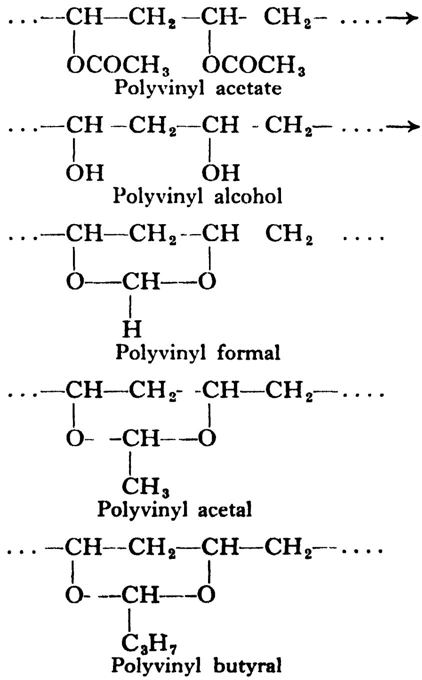


FIG. 99.

stage has been reached a suitable amount of neutralizing agent, e.g. 13 parts concentrated ammonia, is added. The neutralized mass is poured in a thin stream into water. The thread-like material is washed and dried.

While the formal, the acetal, the butyral, etc., are white powders showing no elastic properties, other aldehydes such as furfural give products which are distinctly rubbery. However, when suitably plasticized, the white powders develop marked elastic properties. For example, even the toughest material, high molecular weight polyvinyl formal, when milled with an equal amount of tricresyl phosphate gives a transparent rubbery plastic which can be stretched 300 per cent. and will recover its original shape when the stress is released, although somewhat slowly.

The materials obtained in this way have already attained profound commercial significance. To some extent this has been a measure of the elastic properties. These are most pronounced in the butyral and least in the formal. Films formed from solutions of these materials illustrate the elastic properties. The acetal and the formal can be compounded with plasticizers to give flexible rubbery materials, which can be moulded, extruded, calendered, etc.

The properties of the acetals, or formals, will depend on the extent to which acetaldehyde or formaldehyde respectively have combined and also the state of polymerization. The latter factor will be measured by the viscosity of a standard solution, and will be directly related to the viscosity of the polyvinyl acetate from which the production commences. These features are best illustrated by the characteristics of some of the best-known materials.

TABLE 239. POLYVINYL ACETALS

	Polyvinyl acetate	3 centipoise	7 centipoise	15 centipoise
	Degree of hydrolysis	Softening points		
Polyvinyl	80%	161° C.	191° C.	220° C.
Formal (Formvar)	90%	170° C.	206° C.	250° C.
Polyvinyl	80%	134° C.	170° C.	188° C.
Acetal (Alvar)	90%	143° C.	180° C.	208° C.
Polyvinyl	80%	114° C.	137° C.	149° C.
Butyral (Butvar)	97%	124° C.	146° C.	163° C.

These figures relate to products of the Shawinigan Company.

Polyvinyl formals are soluble in chlorinated hydrocarbons, dioxan, acetic acid and mixtures of benzene and alcohol. They are insoluble in water alcohols, benzene, toluene, petroleum fractions, vegetable oils and so on.

They may be plasticized by the usual materials such as tricresyl phosphate, dibutyl phthalate, benzyl benzoate, with which they are compatible up to 60 per cent.

Polyvinyl acetals are soluble in most organic solvents such as alcohol, benzene, toluene, acetone and chlorinated hydrocarbons. They are insoluble in petroleum hydrocarbons, oils, and so on.

The physical properties are summarized in the following table:

TABLE 240. PHYSICAL PROPERTIES OF POLYVINYL ACETALS

	Formal	Acetal	Butyral
Density at 20° C	1·23	1·14	1·107
Refractive index at 20 C.	1·50	1 446	1·488
Dielectric strength (volts/mil.)	1000	1000	—
Dielectric constant	3·7	2·8	—
Power factor	0·007	—	—
Water absorption (%)	1·3	2 0	4·0

Fillers and colouring matter may be incorporated in the usual manner. These materials have a limited range of application owing to a tendency for cold flow. However, they have found a wide application for a variety of purposes. Polyvinyl butyral was specially designed with the object of providing the interlayer in safety glass. For this purpose it contains a little polyvinyl acetate and polyvinyl alcohol.

Polyvinyl Butyral. Polyvinyl butyrals normally contain less than 2 per cent. of vinyl acetate and 8 to 22 per cent. of vinyl alcohol, the remainder of the molecule being vinyl butyral. Commercial polyvinyl butyral is a white granular flake which coalesces at about 240° F. to a clear, hard, tough solid of a light amber colour. The addition of plasticizer progressively softens the material. Polyvinyl butyral was developed for the interlayer of safety glass as the result of a long, comprehensive, and expensive joint research undertaken by a number of United States concerns. It is already employed for the greater portion of safety glass manufactured in the United States. In this its first use, polyvinyl butyral was plasticized with 40 parts of plasticizer such as dibutyl sebacate. It was then calendered or extruded into sheets 0·015 inch thick. This was used as the inner layer of safety glass.

Polyvinyl butyral is soluble in alcohols, esters, ethylene dichloride,

dioxan, etc. It is insoluble in hydrocarbons, oils, and so on. It may be plasticized by addition of the usual types of materials, e.g. tricresyl phosphate, dibutyl phosphate, dibutyl sebacate, etc. In this manner pronounced elastic properties are developed. Thus the elongation possible may reach 400 per cent. The yield under pressure is very easy and the recovery is slow but nevertheless effective. The softening temperature of the plastic is between 60° and 70° C. The tensile strength attainable is also quite high, being 2500 lbs. per square inch when elongation is 400 per cent., and 8000 lbs. when elongation is only 20 per cent. The flexibility is retained at low temperatures.

It ages well, is unaffected by sunlight, and takes up little moisture. The refractive index, obviously of great importance for application in safety glass, is 1·488, while the light transmission is about 90 per cent.

An interesting development in this field is the application of a vinyl butyral as a substitute for rubber in preparing waterproof fabrics. When car production virtually ceased large amounts of polyvinyl butyral became available for other purposes. Nearly all has gone into coating cloth. Haas has been able to transform the thermoplastic material into a thermosetting one. He developed Saflex,[31] made by Monsanto Chemical Co. The material is applied to fabric by conventional methods used for rubber, by spreading or by calendering. The manipulation and processing of the material is said to present no difficulties. Curing is carried out under the same conditions as apply for rubber.

Polyvinyl butyral is thermoplastic. The first experiments in the cloth-coating field were made with compounds containing resin, fairly large proportions of a suitable plasticizer, pigments, fillers, and a lubricant. Plasticized polyvinyl butyral has a lower softening point than is desirable. These coatings became sticky or even soaked into the fabric at temperatures as low as 160° F. It was necessary to reduce this thermoplasticity.

A number of attempts were made to cross-link vinyl butyral. In 1942 Haas developed the method which made possible a heat-curing material. Although this cross-linking was apparently a condensation reaction, it was physically if not chemically analogous to the vulcanization of rubber. Since that time, many thousands of miles of fabric have been coated in rubber-proofing plants by means of thermosetting vinyl butyral plastics.

Compounding. The compounding agents for vinyl butyral can be divided into five classes—plasticizers, curing agents, fillers, colours, and miscellaneous ingredients such as stabilizers and lubricants. The

amount and type of plasticizer is the main variable in determining flexibility. Esters either of the chemical type such as phthalates, or the vegetable-oil type, such as ricinoleates, are commonly used, and the quantity varies from 30 to 120 parts per 100 parts of resin. Greater nerve and toughness are usually obtained with non-solvent type plasticizers, softness and flexibility with solvent plasticizers ; a mixture of the two types is usually prescribed for a specific application. The plasticized resin must be thoroughly broken down by thorough mastication in internal mixers.

Further compounding follows rubber practice closely and can be readily performed on a rubber mill. Curing agents are selected for the particular purpose required, and are available for cure rates varying from rapid at temperatures as low as 150° F. to slow at 300° F.

Fillers are added either for cheapening or reinforcing. The best filler for simple loading is fine ground whiting, and quantities as high as 100 parts per 100 parts of resin have little effect on physical properties of the stock. For example, adding 100 parts of atomite to a typical stock raised Young's modulus at − 35° C. from 31,000 lbs. to only 40,000 lbs. per square inch, and raised the brittle temperature from − 60° C. to 40° C. It has no effect on tensile strength or elongation at break. Other fillers, such as clay or Silene, dry out the stock with greater toughness and stiffness as a result. Any common filler can be used with no harmful chemical effect on the resin.

Carbon blacks reinforce but not to the extent common in rubber. Fifty parts of lamp black in the stock described above raised the tensile strength from 1200 to 1900 lbs. per square inch, the brittle temperature to − 45° C., and Young's modulus at − 36° C. to 39,000 lbs. per square inch. Common lubricants such as stearic acid are used to help processing.

Processing. Polyvinyl butyral is easy to process on the usual rubber equipment. The average stock runs perfectly on a calender at about 210° F., and no stock requires a higher temperature than 250° F. With the usual curing ingredients the stock can be handled for hours at 220° to 230° F. without scorching but will cure rapidly in the air at 270° F. Frictioning can be performed readily if the centre roll is first wiped thoroughly with a rag dipped in plain milk.

Coatings of pure gum taken from a calender are surface-treated with dust or lacquer exactly as rubber, soapstone and mica being commonly used. Curing of finished fabrics or fabricated articles is best accomplished in hot air, the usual cure being one hour at 260°–270° F.

Extrusion of vinyl butyrals is simple, operating at temperatures used for rubber, e.g. 180°-220° F. Extruding articles can be wrapped and

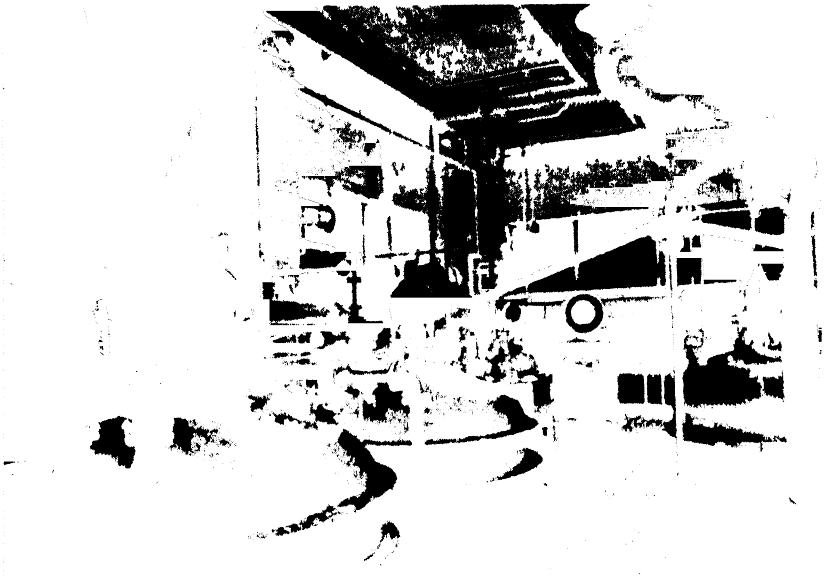


FIG 100—Digesters used in the Preparation of Polyvinyl Butyral

FIG 101—Polyvinyl Butyral formed as a Continuous Rubbery Sheet for use in Safety Glass

cured on mandrels on open steam. Moulding requires special compounding and is facilitated by the use of carbon black, although black is not essential. The butyrals tend to soften rapidly with heat before they set up ; therefore excessive flash is frequently encountered where mould clearances are high. With a cycle of 5–7 minutes at 320°–340°F. good mouldings are obtainable provided the pressure is adjusted to avoid flash. Pieces as complicated as a gas-mask facepiece have been moulded on production lines. Heat-curing butyrals are contrasted to thermoplastic vinyl resins in their ability to be pulled hot from the mould. Moulded sponge of both the open-cell and unicell type can also be made by standard rubber-expanding processes.

Uncured vinyl butyrals are generally soluble in all alcohols. Alcohol solutions may be diluted with naphtha, aromatics, or practically any other solvent to give smoother drying rates and lower cost. Butyral solutions are used for coating of fabrics, casting of film, or preparation of dipped articles.

Fabrication is somewhat troublesome owing to lack of tack. It is necessary to wet surfaces with solvent to obtain tack. Cured polyvinyl butyral is insoluble in all solvents so far tested, so that fabrication is extremely difficult, although air-curing cements with fair strength will adhere to a carefully prepared surface.

Properties. It has excellent abrasion resistance, extreme flexibility, softness and warmth of texture, and good resistance to age, oxidation, and sunlight. Its water absorption is about 3 per cent. The permeation of water vapour is fairly high compared to such materials as Saran. It has poor flex-fatigue life, particularly where flexing is rapid, because it builds up heat when flexed rapidly. The tensile strength varies from 1000 to 3500 lbs. per square inch depending on the compound with corresponding ultimate elongation of 400 to 200 per cent. Tensile strength usually falls off rapidly at temperatures higher than 140° F., but reinforcing blacks assist in maintaining considerable strength up to 200° F. Prolonged exposure to 180° F. has no effect so long as non-volatile plasticizers are used.

Polyvinyl butyral has a tendency to stiffen at low temperatures, Young's modulus changing from 200 lbs. per square inch at + 77° F. to 16,000 lbs. at − 70° F. However, brittle temperatures are usually very low, generally below − 40° F., and some stocks are below − 90° F. The specific gravity of the polyvinyl butyral resin is 1·06 ; finished compounds can run as high as 1·4. Since the covering power and most of the properties are not seriously affected by loading, and since resin cost is high, high loadings are employed.

Colour possibilities are infinite since the base stock is clear and

colourless. The butyral will not yellow in sunlight over long periods of time, and there is also no danger of tendering of fabric or other harmful effects of decomposition. Few solvents, except alcohols and some esters and aromatics, affect the cured product to any degree other than by extraction of plasticizer. In prolonged exposure to aliphatic hydrocarbons there is no swelling, but only a gradual stiffening from plasticizer extraction. The plastic normally supports combustion but can be made to burn very slowly. Vinyl butyrals are sensitive to overcure and tensile strength is rapidly lost, but overcure is far beyond practical cures.

Polyvinyl butyral has been extensively employed for the manufacture of raincoats, water-bags, pontoon boats, food packs and so on, for the use of the United States armed forces. It has also been used as a substitute for rubber in hose-pipes. Its colour possibilities make it of outstanding potential importance in the domestic field for shower curtains, table-cloths and water proofing generally.

Polyacrylic Esters. Acrylic acid has been known for a considerable time. As far back as 1843 Redtenbacher [27] prepared the ethyl ester of acrylic acid. Kahlbaum [18] made the transparent polymer of methyl acrylate in 1880. The methyl, ethyl and propyl esters of acrylic acid were obtained by Weger [37] in 1883. The preparation of numerous other derivatives including acrylic acid amide, the chloride, and the nitrile was carried out by Moureu.[24]

Present-day production is based on the work of Röhm [29] who, in 1901, systematically prepared the solid transparent polymers of the acrylic acid derivatives.[27] Commercial production had to wait until 1931 when successful methods for preparing acrylic esters were developed by Bauer, collaborating with Röhm.[30]

Acrylic ester polymers are chiefly prepared by emulsion polymerization. The liquid monomers are emulsified in water and polymerized by heat or light. The process may be kept under strict control by the addition of cold water. The polymers may be obtained in the form of a stable latex. These emulsions were first described in an I.G. patent in 1931.[17]

Acrylic acid can be esterified with numerous alcohols to give a wide variety of monomers. As the molecular length of the alcohol increases so do the properties of the ultimate polymers become more elastic, the softness, flexibility, heat resistance and water resistance also improving. The properties depend upon the chemical constitution of the monomer and the method employed for polymerization.

The polymerizing conditions largely control the nature of the final product. These may range from hard, tough, thermoplastic materials

to rubbery products, down to semi-fluids. Thus the polymer of methyl acrylate is a tough, pliable, rubber-like substance, films of which may be stretched more than 1000 per cent. The polymers of ethyl acrylate are softer and more elastic. Many of the butyl acrylate polymers are rubbery, but much softer and inclined to be tacky. Methacrylic acid derivatives yield polymers which are much harder, only becoming soft when the amyl esters are formed. They all share certain common properties, they are all thermoplastic, very transparent, resistant to ageing, sunlight or oxygen, and very resistant to chemical attack. They have excellent adhesive properties and are not affected by oils, petrols, or solvents.

In the field of elastic materials the synthetic latex products which give an elastic film have found some application. They dry out to adhesive flexible films, which require no plasticizer. They are widely used for impregnating fabrics, for waterproofing, and for artificial leather. One well-known product is known as Acronal.

One interesting application of dispersions of ethenoid resins has been recently discussed by Nazzaro.[25] This is their use in the preparation of treated paper, which is quite an important commercial commodity. Rubber latex-treated paper was widely used chiefly for making all types of shoes, artificial leather, and for numerous novelty articles. The main applications in shoes were for inner solings, mid-solings, quarter linings, sock linings, etc. Latex, being tough, elastic, and giving a continuous film, was an ideal binder. With the virtual disappearance of rubber latex, and shortages in the supply of reclaim dispersions, it has been found that vinyl and acrylic resin dispersions are extremely satisfactory substitutes. Their effectiveness depends to a great extent on the nature of the plasticizer employed, just as in ordinary compositions. They are particularly successful in association with dispersions of reclaimed rubber. They are also found suitable when employed with quite small proportions of dispersions of synthetic rubbers. A variation of this field of application is in the production of flexible fibre board. The resin emulsions are mixed with the pulp in the usual manner in a beater, and the normal production conditions are employed to produce sheets. This represents a very considerable advance in the scope for these resins.

Solid rubbery materials include the Acryloid resins made in the United States by the Resinous Products and Chemical Co., and Plexigum and Plextol made by the I.G.

The most important part played by acrylic acid derivatives at the present time is as the secondary monomer in the production of butadiene copolymer elastomers.

The methacrylic polymers have, however, attained great importance by virtue of their transparency and amazing transmission of light, Coupled with their great strength and lightness they are extensively employed in aircraft for cockpit covers, windows, instrument panels, etc. They are also able to conduct light round curves and bends, a unique property finding many uses. The leading materials are Perspex in Great Britain, Lucite and Plexiglas in the United States.

Although at present the harder types are employed by virtue of these properties, yet more rubber-like materials with the same optical properties may be anticipated. In which case there may be a perfect combination of the properties of glass and rubber vested in one material.

Another interesting application, where acrylic resins already compete successfully with a rubber product, is for dentures.

The first patent obtained by Rohm, who pioneered the industrial exploitation of acrylic resins, was concerned with making artificial rubber. Rohm prepared his rubber substitute by mixing a polymerized acrylic ester with sulphur and "vulcanizing" the mixture at about 40° C. for 2 hours. The mechanism and nature of this vulcanization of essentially saturated acrylic polymers was not described.

Rohm and Bauer described the preparation of acrylic resin mixtures containing mineral fillers and other materials which they claimed were suitable for the manufacture of skid-proof tyres. According to the reports of other investigators rubber-like materials have been made by the emulsion polymerization of acrylic esters, and the rubber-like properties of acrylic resins have been enhanced by the admixture of tannic acid, ferric acetate, copper powder, and antimony potassium tartrate.

Nowak claimed that vulcanization does not occur when polyacrylic esters and sulphur mixtures are heated unless a surface catalyst such as carbon black is present. His process of making rubber-like materials consisted in incorporating sulphur, β-naphthol, carbon black, and talc into polymerized ethyl acrylate by milling at 90 to 110° C.

Vulcanization of acrylic polymers having olefinic unsaturation has been mentioned briefly. Mark and Fikentscher prepared a polymer of allyl acrylate by treating polyacrylyl chloride with allyl alcohol, and stated that vulcanization transformed it into rubber-like products. The copolymers of vinyl β-methylcrotonate and an acrylic ester have been vulcanized with sulphur, presumably by virtue of unsaturation furnished by the vinyl β-methylcrotonate.

Lactoprenes. Recently a new group of elastic materials has been developed based on acrylic esters. The work has been carried out at the Eastern Regional Laboratories of the United States Department of

Agriculture. They owe their name to the fact that the key material in their production is lactic acid. The materials are of outstanding interest from the viewpoint that they can be derived readily from certain waste agricultural products, from carbohydrates and from some other natural minerals. These include whey, molasses, corn, sugar, petroleum and coal. So far as carbohydrates are concerned the quantity which can be obtained is twice as much as the amount of butadiene derivatives. Smith, Fisher, Ratchford and Fein [34] have shown how carbohydrates can be converted to acrylic esters by the following steps:

(*a*) fermentation production of lactic acid,
(*b*) esterification of lactic acid with methanol,
(*c*) acetylation of methyl acrylate,
(*d*) pyrolysis of acetylated methyl acrylate.

Mast, Rehberg, Dietz and Fisher [23] have described the proportion of vulcanized materials based on acrylic resins. They copolymerized ethyl acrylate with small proportions of acrylonitrile, *m*-cyanoethyl acrylate, etc. The rubber-like polymers obtained were usually tacky and quite easily handled on mixing rolls. They then proceeded to vulcanize the materials with reagents such as benzoyl peroxide, sulphur and organic accelerators, *p*-quinone-dioxime, and red lead, etc.

They were able to vulcanize polyethyl acrylate with benzoyl peroxide, but obtained rather better products with quinone dioxime. They found that many of these materials were vulcanizable with sulphur accelerator mixtures. The advantages they obtained by vulcanizing these materials were summarized as follows:

(*a*) There is no necessity to use special methods to prevent cross-linkage.
(*b*) Both polymers and copolymers are soluble and the viscosity of the solutions give indications of the molecular weight.
(*c*) Synthetic rubber-like cements can be prepared readily.

The vulcanized materials are resistant to oxygen and ageing and towards paraffinic oils. The materials can be compounded with the usual range of reagents, and interesting materials were obtained.

Mast, Smith and Fisher copolymerized ethyl acrylate with small amounts of allyl maleate. The materials obtained were vulcanized with various reagents and gave interesting results. Non-sulphur vulcanizing gave the best results. The amount of allyl maleate employed ranged between 1 per cent. and 5 per cent.

Fisher, Mast, Rehberg and Smith [12] investigated the behaviour of

TABLE 241. VULCANIZATION OF POLYETHYL ACRYLATE AND ETHYL ACRYLATE COPOLYMERS [a]

Copolymerizing monomers, %	Compounding recipe	Curing time at 298° F., min.[b]	Tensile strength lb. per sq. in.	Ultimate elongation, %	Shore A hardness	Tensile product	Brittle point, ° C.
None	Quinone dioxime[c]	240	1390	510	55	710	− 16
	Benzoyl peroxide[d]	120	810	440	46	355	− 16
	Sulphur[e, f]	—	—	—	—	—	—
Acrylonitrile, 5	Quinone dioxime[c]	240	1320	260	72	345	− 11
	Benzoyl peroxide[d]	180	1000	420	53	420	− 7
	Sulphur[e]	240	830	1040	50	860	− 7
Acrylonitrile, 5	Quinone dioxime[c]	240	1420	340	70	480	− 9
	Benzoyl peroxide[d]	120	870	520	52	450	8
	Sulphur[e, f]	—	—	—	—	—	—
β-Chloropropyl acrylate, 4·8	Quinone dioxime[c]	150[h]	1610	470	67	756	—
	Sulphur[e]	210[i]	1240	950	39	1178	—
β-Chloroethyl acrylate, 5	Quinone dioxime[c]	120	1610	400	64	645	− 15
	Benzoyl peroxide[d]	240	870	500	45	435	9
	Sulphur[e]	240	1280	880	46	1125	− 15
β-Chloroethyl acrylate, 10	Quinone dioxime[c]	180	1350	460	56	620	− 15
	Benzoyl peroxide[d]	120	1050	280	50	295	− 11
	Sulphur[e]	180	1220	720	42	880	− 14
β-Chloroethyl acrylate, 5; acrylo-nitrile, 6	Quinone dioxime[c]	240	1180	470	56	555	− 5
	Benzoyl peroxide[d]	180	820	560	45	460	− 6
	Sulphur[e, f]	—	—	—	—	—	—
Benzyl acrylate, 5	Quinone dioxime[c]	240	1410	480	65	675	− 11
	Benzoyl peroxide[d]	120	640	490	45	315	− 10
	Sulphur[e]	240	100	2400	40	—	—
Phenyl acrylate, 5	Quinone dioxime[c]	240	960	180	75	170	− 17
	Benzoyl peroxide[d]	20	570	480	42	275	− 11
	Sulphur[e]	240	790	780	50	615	− 16
Methoxyethyl acrylate, 5	Quinone dioxime[c]	240	1090	340	55	370	17
	Benzoyl peroxide[d]	80	100	380	40	—	—
	Sulphur[e]	240	100	680	39	—	—
β-Cyanoethyl acrylate, 5	Quinone dioxime[c]	120	1670	450	65	750	− 15
	Benzoyl peroxide[d]	80	510	440	45	225	− 13
	Sulphur[e]	120	1090	860	48	940	− 16
2-Me-2-nitro-1-propyl acrylate, 5	Quinone dioxime[c]	120	470	410	31	190	− 14
	Benzoyl peroxide[d]	180	760	440	41	335	− 13
	Sulphur[e, f]	—	—	—	—	—	—

[a] Prepared by emulsion polymerization.
[b] Cured in 4 × 4 × 0·032-inch moulds.
[c] Compounded: polymer, 100; red lead, 10; quinone dioxime, 2; zinc oxide, 5; stearic acid, 3; Furnex beads (semi-reinforcing carbon black), 30.
[d] Compounded: polymer, 100; iron oxide, 150; Luperco A (benzoyl peroxide), 5.
[e] Compounded: polymer, 100; Captax (mercaptobenzothiazole), 0·5; zinc oxide, 10; stearic acid, 2; sulphur, 2; Furnex beads, 30; Tuads (tetramethylthiuram disulphide), 1.
[f] Specimen unsatisfactory for testing.
[g] Cured in 6 × 6 × 0·075-inch moulds.
[h] Cured at 303° F.
[i] Cured at 312° F.

acrylic ester polymers containing small quantities of polyfunctional monomers, such as butadiene, isoprene, and allyl maleate. Soft rubber-like copolymers were produced under certain conditions which could be readily mixed with fillers, sulphur and accelerators. The compounds formed were then vulcanized and interesting materials were obtained. The vulcanized materials were extremely rubber-like.

Various types of acrylic elastomers have been made by polymerizing different acrylic esters, $CH_2{:}CH\ COOR$. Ethyl acrylate has been used in most instances, however, and most attention has been given to copolymers made by polymerizing ethyl acrylate with a small quantity of a halogen-containing monomer such as 3-chloropropyl acrylate ($CH_2{:}CHCOOCH_2CH_2CH_2Cl$) or 2-chloroethyl vinyl ether ($ClCH_2CH_2OCH{:}CH_2$). Lactoprene EV is made by polymerizing an emulsified mixture of 95 per cent. ethyl acrylate and 5 per cent. chloroethyl vinyl ether. Although it cures somewhat more slowly than the corresponding ethyl acrylatechloropropyl acrylate copolymer it is generally similar in other respects. Lactoprene EV presumably has the following chain structure:

$$
\begin{array}{cccccccc}
 & & & COOC_2H_5 & & & & COOC_2H_5 \\
 & & & | & & & & \\
-CH_2- & CH & -CH_2- & CH & -CH_2 & CH & -CH_2- & CH- \\
 & | & & & & & & \\
 & COOC_2H_5 & & & & OCH_2CH_2Cl & &
\end{array}
$$

Special Properties and Advantages of Lactoprene. In describing the properties and potential uses of lactoprene, it is compared with standard GR-S. The advantages and disadvantages of lactoprene are summarized as follows:

Comparison of Lactoprene EV with Standard GR-S Rubber. Highly superior or advantageous to GR-S with respect to:

1. Flex Life.
2. Oil resistance.
3. Resistance to oxidation and ageing at normal and elevated temperatures.
4. Resistance to sunlight.

Superior or advantageous with respect to:

1. Permeability to hydrogen, helium, and carbon dioxide.
2. Retention of elongation at high temperature.
3. Abrasion resistance (according to limited available data).
4. Ease and simplicity of production.
5. Yield from carbohydrate sources.
6. Suitability for production of white stocks or articles having pastel shades.

Equal with respect to:

1. Ease of pigment incorporation.
2. Variety of curing recipes and rate of curing.

3. Retention of tensile strength at 212° F.
4. Permanent set.
5. Resilience at 212° F.

Inferior with respect to:

1. Tensile strength at normal temperatures (slight when compared with similarly loaded GR-S).
2. Retention of modulus at 212° F. except in the longer cures.
3. Compression set (slight).
4. Heat build-up (except for higher cures).
5. Resilience at room temperature.
6. Flexibility at low temperatures (but sufficiently flexible—if plasticized—at temperatures normal in civilian applications).
7. Resistance to steam.
8. Swelling in water (although undesirable for some applications, this characteristic might be advantageous for the manufacture of rubber sheets, shoes, garments, etc.).
9. Cost (acrylic esters are made on a relatively small scale, but it is confidently expected that the price of acrylic esters will be substantially lowered).

According to Fisher, although butadiene rubbers and acrylic elastomers are structurally similar in having a long carbon chain, the butadiene chain has olefinic linkages and no ester groups; whereas the acrylic chain has ester groups but no olefinic linkages. A portion of a butadiene polymer chain may be written as

$$\text{—}CH_2CH{:}CHCH_2CH_2CH{:}CHCH_2\text{—}$$

whereas the lactoprene polymer chain is represented as

$$
\begin{array}{cccccccc}
 & & & \mathrm{COOR} & & & & \mathrm{COOR} \\
 & & & | & & & & | \\
\text{—}\mathrm{CH_2} & \mathrm{CH}\text{—} & \mathrm{CH_2} & \mathrm{CH}\text{—} & \mathrm{CH_2} & \mathrm{CH}\text{—} & \mathrm{CH_2} & \mathrm{CH}\text{—} \\
 & | & & & & | & & \\
 & \mathrm{COOR} & & & & \mathrm{COOR} & &
\end{array}
$$

These structural features have a direct bearing on the properties of the raw polymer and the vulcanizates. The olefinic linkages, needed for the vulcanization of butadiene polymers and natural rubber, facilitate oxidation and are largely responsible for deterioration and ageing. Not having olefinic linkages, lactoprene is resistant to oxidation and weathering. The oxygen-containing ester groups in lactoprene are probably responsible for its oil resistance.

Potential Uses. Lactoprene naturally should prove most useful

in fields in which its special properties are used to the maximum. Because of its excellent flex life, cut-growth resistance and resistance to oils, oxidation, and deterioration at normal and elevated temperatures, lactoprene should be useful, possibly preferable to other elastomers, for products such as hose, gaskets, and packings, transmission and conveyor belts, boots, soles, and heels which come in contact with oil or heat, tank linings where oil or high temperatures are encountered, printing rolls, white articles or articles having pastel shades, oil-resistant gloves and fabrics, machine and instrument supports, grommets, mats, and pads, protective covers, cements, gasoline hose nozzles, coated cloth and paper (applied from solution or water emulsion), and laminated paper and cloth.

Lactoprene has been experimentally used as latex and as rubber cement. Hard rubber-like materials have been made from lactoprene. More data are needed, however, to assess the merit and possibilities of lactoprene in these fields.

REFERENCES

[1] Barron, Dean and Scott, *Trans. I.E.E.*, 1944, **91**, 297.
[2] Baumann, *Ann.*, 1872, **163**, 308.
[3] Benedito, *British Plastics*, 1943, **15**, 175.
[4] British-Thompson-Houston Co., Ltd., B.P. 518,006/1936.
[5] Brous, U.S.P. 2,234,621/1940.
[6] Brous and Semon, *Ind. Eng. Chem.*, 1935, **27**, 667.
[7] Buchmann, *Kunstoffe*, 1940, **30**, 357.
[8] Carbide and Carbon Corp., U.S.P. 1,775,882.
[9] Douglas, *Ind. Eng. Chem.*, 1936, **28**, 1125.
[10] Du Pont de Nemours, B.P. 319,887/1928.
[11] Fairweather, B.P. 539,834/1941.
[12] Fisher, Mast, Rehberg and Smith, *Ind. Eng. Chem.*, 1944, **36**, 1033.
[13] Fuoss, *J. Amer. Chem. Soc.*, 1938, **60**, 451 ; 1938, **60**, 456 ; 1939, **61**, 2329 ; 1939, **61**, 2334.
[14] Goggin and Lowry, *Ind. Chem. Eng.*, 1942, **34**, 327.
[15] Herrmann and Haenkel, *Berichte*, 1927, **60**, 1658.
[16] I.G., G.P. 362,366.
[17] I.G., B.P. 358,534/1931.
[18] Kahlbaum, *Berichte*, 1880, **13**, 2348.
[19] Klatte, G.P. 281,687/1912.
[20] Klatte and Rollett, U.S.P. 1,241,738/1917.
[21] Lawson, B.P. 319,588/1929.
[22] Mast, Dietz, Dean and Fisher, *India Rubber World*, 1947, **116**, 355.
[23] Mast, Rehberg, Dietz and Fisher, *Ind. Eng. Chem.*, 1944, **36**, 1022.
[24] Moureu, *Bull. Soc. Chim.*, 1893, **9**, 386.
[25] Nazzaro, *India Rubber World*, 1942, **106**, 345.
[26] Ostromislensky, G.P. 264,123/1912.
[27] Redtenbacher, *Ann.*, 1843, **47**, 113.

[28] REGNAULT, *Ann. chim. phys.*, 1838, **65**, 157.
[29] RÖHM, *Berichte*, 1901, **34**, 593.
[30] RÖHM and BAUER, G.P. 656,421/1939; 693,140/1940.
[31] Saflex, *India Rubber World*, 1942, **106**, 599.
[32] SCHOENFELD, BROWNE and BROUS, *Ind. Eng. Chem.*, 1939, **31**, 964.
[33] SEMON, U.S.P., 1,929,453/1933.
[34] SMITH, FISHER, RATCHFORD and FEIN, *Ind. Eng. Chem.*, 1942, **34**, 473.
[35] VON PECHMAN and RÖHM, *Berichte*, 1901, **34**, 427.
[36] Vinylidene Chloride—Dow Chemical Co. Technical literature.
[37] WEGER, *Ann.*, 1883, **221**, 79.
[38] C.I.O.S., XXXIII–23.
[39] C.I.O.S., XXVIII–13.
[40] C.I.O.S., XXII–1.
[41] C.I.O.S., XXVI–185.

CHAPTER 21

MISCELLANEOUS SYNTHETIC ELASTICS—ETHYL CELLULOSE—ESTER RUBBERS

THERE are a number of cellulose plastics which have been widely used chiefly by virtue of their toughness and flexibility. The most important is of course cellulose acetate. However, ethyl cellulose has in recent years attained some importance. There has been a realization that ethyl cellulose compositions could be prepared which were distinctly elastic and rubber-like. This particular aspect has been greatly developed since the rubber shortage became acute and substitutes were necessary. It has attained sufficient importance for this application as to justify inclusion among synthetic elastic materials. In the United States compositions based on ethyl cellulose have been described as ethyl rubber.

It has been manufactured on quite a large scale for some years both in the United States and in Germany. In 1946 American production exceeded 12 million lbs. The leading producers in the United States include the Dow Chemical Co., the Hercules Powder Co., Celanese Corporation, etc. It has long been manufactured in Germany by the I.G. Farbenindustrie. In Great Britain until recently there has not been any notable interest in this material.

Ethyl cellulose is of much more recent derivation than the older better-known cellulose esters such as cellulose nitrate and cellulose acetate. Chemically it is rather different, inasmuch as it is a substitution product of cellulose, an ether, whereas the others are essentially esters. Methods for preparing ethers of cellulose were described, almost simultaneously in 1912 by Dreyfus,[3] Leuchs,[5] and Lilienfeld.[6]

It is for this reason that ethyl cellulose possesses greater chemical stability than either of the other materials. By virtue of being based on cellulose, it has a number of outstanding properties. For example, it is extremely flexible, it has great toughness, it has a high degree of thermoplasticity, it does not tend to age, is unaffected by sunlight, and it maintains its strength at very low temperature. These characteristics are favourably affected by the addition of suitable compounding ingredients.

Production of Ethyl Cellulose. Ethyl cellulose is manufactured from cotton linters or from wood cellulose by the action of ethyl chloride or ethyl sulphate. Cellulose itself is now considered to be

composed of long-chain molecules composed of units of glucose residues having an empirical formula $C_6H_{10}O_5$. Each unit has three reactive hydroxyl groups which can be substituted. Ethyl cellulose is the product obtained when an ethyl group has replaced the hydrogen in these hydroxyl groups. This need not be carried to completion, partial substitution taking place. The extent to which substitution has been carried accounts for the ability to obtain derivatives having somewhat different characteristics. In the production of commercial materials ethyl cellulose is never fully substituted, there being only from 2 to 2·5 ethoxyl groups present in each glucose unit.

It is interesting to notice that cellulose derivatives have a long-chain structure of repeating units, in this respect resembling rubber.

The actual preparation of ethyl cellulose involves the treatment of cellulose, in the form of cotton linters, with a strong solution of sodium hydroxide. Alkali cellulose is formed in this manner. The appearance of the cotton linters is not substantially changed. This alkali cellulose is then treated with gaseous ethyl chloride under pressure. In this process the ethyl group replaces the sodium atom and forms ethyl cellulose. The manufacturing conditions are kept under very careful control so that the reaction may proceed without undue degradation of the cellulose, and incidentally with the greatest economy of alkylating agent. When the reaction has been completed the product is washed with large quantities of water so that water-soluble ingredients are completely removed.

Different Grades of Ethyl Cellulose. A number of grades of ethyl cellulose may be obtained according to the degree to which alkylation has been carried. These are differentiated by reference to the ethoxyl content possessed by each type. For example, the Hercules Company markets five types, as follows [4]:

T—48·5—50% ethoxyl content
N—46 8—48 5% ethoxyl content
K—45·5—46–48% ethoxyl content
G—44·5—45·5% ethoxyl content
D—43·5—44·5% ethoxyl content

The Dow Chemical Co. markets the following types:

TABLE 242. SOFTENING POINTS OF ETHOCEL TYPES [2]

Ethoxy type	Ethoxy content: Mols per C_6 unit	Ethoxy content: %	Softening temp. ° C.	Melting temp. ° C.
Low	2·25–2·25	43·5–45·0	180–160	200–210
Medium	2·25–2·46	45·0–48·0	160–140	200–210
Standard	2·46–2·58	48·0–49·5	140–160	200–210

The more completely substituted materials, containing between 48 and 49·5 ethoxyl, are more widely soluble, have a higher water resistance, a lower softening point, and are more compatible with other materials. They are not as tough as the materials containing lower proportions of ethoxyl.

Apart from the ethoxyl content of the material there can be a variation of viscosity in each instance, which has a profound affect on the properties of the material. It must be clearly understood that ethoxyl content refers to chemical composition, while viscosity is quite different, being a function of the structure. In other words, viscosity is primarily a function of molecular weight or the number of glucose units which comprise the average chain length of the particular derivative. The viscosity will vary, therefore, depending upon the mechanical treatment to which the cellulose has been submitted, and the degree of degradation that has been permitted to take place during production. Commercial materials are therefore supplied in a range of different viscosities corresponding to each particular ethoxyl content. Plastics and films made of high-viscosity materials are usually much tougher and stronger than those made from low-viscosity materials.

Properties of Ethyl Cellulose. Ethyl cellulose has the lowest specific gravity of any of the cellulose derivatives available commercially. Its density is 1·14, so that the cost per unit of volume for any product is comparatively low.

Films may be cast from solutions of ethyl cellulose, and in the form of films ethyl cellulose has exceptional toughness. This strength is retained over a wide range of temperatures. What is important is the fact that even at extremely low temperatures, for example, $-40°$ F., ethyl cellulose films are extensible and resistant to shock.

Ethyl cellulose has exceptionally good electrical characteristics, not only possessing a high insulation strength and low specific inductive capacity, but it also has a relatively low power factor. The significance of these properties is enhanced by its comparatively low water absorption which may be further improved by suitable compounding. It is resistant to acids and alkalis.

Ethyl cellulose is soluble in most organic liquids. In fact, the only solvents which do not appear to affect it are straight-chain petroleum hydrocarbons. The best solvent combination for preparing solutions comprises 70 to 80 parts by weight of an aromatic hydrocarbon such as toluene or solvent naphtha, together with 30 to 20 parts of aliphatic alcohol such as ethyl alcohol. Such solutions are easily made, and may be handled without difficulty.

Plasticizers. In a similar manner ethyl cellulose is compatible

with a very large number of plasticizers and modifying agents. True plasticizers include such materials as esters, and chlorinated diphenyls. Outstanding among these are the following materials : tributyl phosphate, tricresyl phosphate, triphenyl phosphate, diethyl phthalate, dibutyl phthalate, diamyl phthalate, butyl stearate, amyl stearate, amyl oleate, dibutyl sebacate, benzyl benzoate, triacetin, sulphonamide plasticizers, chlorinated diphenyl, etc. In addition, all fatty acids are miscible with it such as castor oil, stearic acid, oleic acid, etc. ; and fatty alcohols such as lauryl alcohol, cetyl alcohol, etc. ; in addition to these, castor oil, linseed oil, liquid paraffin, etc., and the corresponding blown oils, are all compatible, and act as plasticizers for ethyl cellulose.

Extenders. Ethyl cellulose, by virtue of its compatibility with many types of resins, may be extended by their use. For example, it is miscible with alkyl resins and alcohol-soluble resins, e.g. natural resins and gums, rosin, phenol-formaldehyde, ester gum, etc.

Apart from these characteristics, it is compatible with all proportions of cellulose nitrate, although it does not mix with cellulose acetate, nor with chlorinated rubber. One of its outstanding characteristics is the fact that it dissolves readily in hot resins, oils, waxes, plasticizers, and mixtures of these. By use of this property, thermoplastic compositions may be prepared which can be applied in the molten condition, and form a basis for adhesives, coatings, etc.

One of the outstanding advantages of ethyl cellulose is its exceptional heat stability. This implies that full advantage can be taken of its thermoplastic character, in contrast to the critical behaviour of polyvinyl chloride. This stability is also well shown by the fact that ethyl cellulose may be melted together with many oils and waxes. It has outstanding resistance to all concentrations of alkalis and is resistant to dilute acids. It is odourless and tasteless.

Ethyl cellulose is easily and smoothly converted into a thermoplastic rubber-like material. This is achieved by mixing with plasticizers in a Banbury mixer, or on open rolls. High working temperatures are employed, comparable with those used with polyvinyl chloride. Fairly large proportions of plasticizers, 50 volumes and upwards, are necessary to give useful extrusion compounds.

As is the case with other plastics the addition of plasticizers causes the range of plastic properties to move up and down the temperature scale. In other words, with high plasticizer additions extremely rubbery compounds are attainable which retain their flexibility at very low temperature, but at the cost of low deformation temperatures in the upper range, and vice versa. Although the electrical character-

istics of ethyl cellulose are extremely good, they are considerably affected by the nature of the plasticizer.

Rubbery Materials. Ethyl cellulose compositions may be handled on standard rubber plant, although rather higher temperatures are necessary than with rubber. The material may be calendered, extruded, and generally processed along the lines normally employed with rubber, allowances all the time having to be made for higher temperatures.

The following mixes give typical examples of compositions which have marked elastic characteristics.

TABLE 243. ETHYL CELLULOSE COMPOSITIONS

(*a*)	Ethyl cellulose	100
	Chlorinated diphenyl	100
(*b*)	Ethyl cellulose	100
	Tricresyl phosphate	75
(*c*)	Ethyl cellulose	100
	White paraffin oil	40
(*d*)	Ethyl cellulose	100
	Raw castor oil	15
	Dibutyl phthalate	15
	White paraffin oil	25
	Titanium dioxide	1
	Oil soluble red	0·3

The following table illustrates some typical flexible materials having elastic characteristics :

TABLE 244. PROPERTIES OF ETHYL CELLULOSE

	Pure film	Flexible plastic
Density	1·14	1·05
Refractive index	1·47	—
Resistivity (ohms/cms.)	10^{11}	10^{14}
Dielectric strength (volts/mil.)	1500	750
Dielectric constant—		
25° C. 1000 cycles	3·0	—
60 „	2·6	2·7
Power factor—		
25° C. 1000 cycles	0·0025	—
60 cycles	0·0030	0·006
Tensile strength (lb./in.^{2})	8000	3000
Elongation (%)	15	90
Softening point	150° C.	80° C.
Melting point	200° C.	—
Water absorption (48 hrs. immersion)	4%	5·0%
Crack point	—	− 55° C.

One of the outstanding features of ethyl cellulose compositions is that they are relatively insensitive to high temperatures. That is to say, that although they become plastic and flow the materials are not decomposed at fairly high temperatures up to 200° C. Almost the

outstanding property is the fact that suitably compounded materials retain their flexibility to extremely low temperatures. For example, compositions may be prepared which will still be flexible at $- 70°$ C. This has opened up a number of useful applications for the material.

TABLE 245. PROPERTIES OF TYPICAL ETHYL CELLULOSE PLASTICS [7]

	Ethyl cellulose A			Rubber	
		II	III	Dipped article	Inner tube
Water Absorption:					
Percentage of original weight after 24 hrs.	105·1	104·9	104·2	112·8	100·9
Percentage of original weight after 48 hrs.	105·3	111·5	104·9	115·3	101·1
Percentage of original weight after 70 hrs.	106·0	112·8	106·3	117·6	101·2
Dimensional Stability in Boiling Water:					
Percentage of original length after 10 mins.	98·0	99·5	—	102·0	100·0
Percentage of original width after 10 mins.	101·0	101·0	—	103·9	100·0
Percentage of original thickness after 10 mins.	104·0	103·6	—	100·0	100·0
Appearance after removal from water	c	wh	—	Opaque initially	Opaque initially
Dimensional Stability in Water at Room Temperature:					
Percentage of original length after one week	102·4	107·6	—	110·0	101·0
Percentage of original width after one week	103·0	107·5	—	109·2	100·0
Percentage of original thickness after one week	106·2	107·3	—	112·5	101·5
Shore Hardness:					
Shore values	31	29	27	Sample too thin	90
Tensile Strength:					
Pounds per cross-sectional sq. in.	1700	1170	2290	4500 [a]	3500 [a]
Percentage Elongation	103	86	123	760	575
Permanent Set:					
Percentage of total stretch retained from quick tension, 21° C. (Scott tester Dh-2)	9	6	24·2	0	0
Percentage total stretch retained from slow tension, 21° C.	11·5	81	—	0	0
Percentage total stretch retained from slow tension, 50° C.	100	100	—	0	0
Flexibility at $-20°$ C.:					
Number double folds (M.I.T. Flex Tester)	170	No sample	97	65,000 +	Sample too thick
Flexibility at Approximately $-78°$ C.:					
(Pinch test)	brittle	flexible	brittle	flexible	brittle
Burning Rate:					
Seconds for 3-in. length	71	28	—	20	66

Identification of materials tested:

A-Ethyl cellulose, Grade "N" used (46·8 to 48·5 ethyl content, 100 centipoise viscosity).

Composition, Col. I: Ethyl cellulose.
Raw castor oil.

Col. II: Ethyl cellulose.
Cotton-seed oil.
Raw castor oil.

Col. III: Ethyl cellulose.
Raw castor oil.
Opal wax.

[a] Author's figures. c = colourless. wh = white

The applications of ethyl cellulose have hitherto been mainly confined to the preparation of lacquers, varnishes and adhesives, and as modifying agents for waxes and resins. It has been increasingly utilized for the preparation of plastics which are moulded both by compression and injection. Suitable compounding enhances the flexibility and extensibility of the material to such an extent that it is being widely used to replace rubber. By virtue of the excellent electrical characteristics the high flexibility and toughness, ethyl cellulose compositions are widely employed for wire insulation and similar applications. Fillers, plasticizers, and colouring materials may be added to ethyl cellulose. The best filler is zinc oxide when used up to 30 per cent. loadings. Other fillers may be incorporated, but heavy loadings detract from the performance. Ethyl cellulose compositions are ordinarily transparent, but by the use of suitable pigments a complete range of colours may be obtained, either transparent, translucent, or opaque.

Wiggam [7] has made a comparison of ethyl cellulose compositions with rubber compounds. He pointed out that their handling differs from that used with rubber, in particular vulcanization being unnecessary. Processing is much more rapid with consequent higher production. He found that in some properties they were superior to rubber. Abrasion could be made better, they were resistant to ozone and to oils and petrol. On the other hand they had very little resilience or " bounce ".

Paracon. Some interesting products with possibilities have been developed in the field of polyesters. The Paracon group of materials comes in this field. They had been developed in the Bell Laboratories. At the present time only one has assumed any significance, namely, Paraplex X.100, made by Resinous Products in the United States. This has good resistance towards oil and petrol, being comparable to the Perbunan type of material.

Long-chain dibasic acids are used to prepare Paracons of low brittle points, while short-chain acids with high oxygen-to-carbon ratio give products resistant to oil. It is a yellow, wax-like material, specific gravity 1·08 with a characteristic mild odour. It has a relatively sharp melting-point of about 40° C., which means that storage conditions must be carefully watched. It is soluble in organic solvents such as benzene and other aromatic solvents, chloroform, ethylene dichloride, and so on.

Compounding is complicated by the tendency to stick to the rolls. Carbon black is not employed with this material, the filler generally employed being whiting or treated whiting. The only other normal

addition to a mixing is about 1 per cent. of paraffin wax to help processing. Vulcanization is carried out by means of addition of 1 per cent. benzoyl peroxide. Tensile strength of properly compounded materials average 1700 lbs. per square inch, while elongation is about 400 per cent.

A typical mixing is the following—

Paraplex X.100	100 parts
Wax	1 part
Calcium carbonate	100 parts
Benzoyl peroxide	1 part

Vulcanization usually takes 10 minutes at 125° C. There is little tendency to overcure.

Tensile properties of the compound above are:

T_B	125 kg. per sq. cm.
Elongation	350
M.200	100 kg. per sq. cm.
H.75	Resilience 63

It can be formed into doughs with benzene and spread. It is resistant towards oxygen and stands up to heat-ageing up to 120° C. comparatively well.

The material has the following electrical characteristics:

Volume resistivity, 2×10^{11}
Power factor at 800 cycles—0·87
S.I.C.—6·5

Paracons have relatively low resistance towards acids, alkalis and steam.

Paracon gums are suggested for special tubing, gaskets, adhesives, binders and ignition cable coverings.

Biggs, Erickson and Fuller [1] have described useful vulcanizable polyesters derived from dibasic acids and propylene glycol.

Preparation of Norepol. Quite a number of synthetic rubber-like materials have appeared in recent years based upon vegetable oils, and come into the chemical class of polyesters. They are all more or less similar. Oils used include soya-bean oil, corn oil, linseed oil, and so on. These are combined with a suitable glycol and then polymerized. Norepol is a typical example about which there is a fair amount of information.

Norepol is the name given to a high molecular weight polymer produced from vegetable oils which contain substantial quantities of linolein acid. Very briefly the material is produced by the controlled

polymerization of the ethylene glycol ester of the dimer or linoleic acid to viscous high molecular weight material. The viscous polyester may be transformed into a product capable of being handled on a rubber mill by further heating with sulphur and accelerating agents or by further polymerization through agitation with heat in an internal mixer. The material is not very easy to handle.

The product so obtained may then be compounded in any manner desirable to obtain an end product with given physical characteristics. A typical compound is—

Norepol	100
P.33	80
S.	12
Zinc oxide	6
M.B.T.S.	2
Phenyl-β-naphthylamines	1

Cured at 141° C. for 30 minutes.

The final finished rubber product may have tensile strengths ranging from 200 to 800 lbs. per square inch, and elongations ranging from 100 to 250 per cent., depending upon the composition and conditions.

Laboratory experiments have yielded examples of Norepol having tensile strengths of over 2,000 lbs. per square inch and elongations ranging up to 500 per cent.

The material has a number of disadvantages for straightforward use as a rubber. It has low tensile strength. It tends to be soft and plastic with high set. It does not age very well, nor will it stand up to heat. While it has fair resistance towards alpihatic oils and solvents it will not stand up to aromatic solvents nor to vegetable oils. It has found some use as an extender and diluent for other types of material.

One hundred lbs. of soya-bean oil will yield approximately 40 lbs. of Norepol polyester, and around 9 lbs. of glycerol with the remainder of the oil represented by recoverable crude fatty acids. Forty lbs. of Norepol polyester would yield from 60 to 80 lbs. of finished rubber goods, depending upon the particular compounding formula used and, of course, also on the type of finished goods desired.

Vulcaprene A—or S.R.E.[8] Vulcaprene A is a special synthetic rubber produced by Imperial Chemical Industries, Ltd. It is a light-coloured product which when milled resembles crepe rubber. It has good tack. The specific gravity is 1·15. The composition has not yet been disclosed. All that is known is that it differs from the butadiene copolymers in so far as sulphur is not employed for vulcanization. It can only be kept in storage for three months and it tends to harden up in a few days if allowed to stand after milling.

It is readily mixed with compounding ingredients. However, vulcanization or setting is retarded by alkaline materials and these must be carefully avoided in using Vulcaprene. Inert fillers are usually employed. While carbon black imparts good tensile characteristics, very satisfactory physical properties can be obtained with light-coloured fillers.

Vulcanization is carried out with special chemicals the nature of which has not yet been disclosed. Proprietary materials are supplied thus:

(*a*) For moulding, extrusion, calendering, and sheeting, Vulcafor VHN and Vulcafor VDC are used.

(*b*) For spreading purposes Vulcafor VDN and Vulcafor VBN are employed.

Two-stage vulcanization is necessary. Generally a 25-minute press cure is followed by a further baking period of 2 hours at 125° C. in air. The material is extremely good, solvent resistant towards mineral oils, aliphatic oils, and vegetable oils. It will not stand up to steam aromatic solvents and chlorinated solvents.

It has been recommended for petrol hose, oil hose, printers' blankets, diaphragms, gaskets, and seals generally. It is extremely impermeable to gas and has possibilities in this direction. While it withstands dry heat fairly satisfactorily it breaks down after some weeks at 100° C. and breaks down very rapidly at high temperatures. It has a low freezing temperature of about 35° C.

Behaviour of typical mixes is illustrated in the following examples:

Composition of Mix

Vulcaprene A	100
Dark substitute	10
SRF	45
Vulcafor VHM	5
Vulcafor VDC	0·75
Stearic acid	0·75

A very interesting field of application for these materials is for synthetic finishes. Brightly coloured lacquers are now available which are especially suited for application to rubber surfaces. They are cured by addition of a setting agent before application. The adhesion to vulcanized rubber even when stretched is exceptionally good.

TABLE 246. CHINA CLAY MIXES

Volume loading of china clay	0	10	20	30	40	50
Vulcaprene A	100	100	100	100	100	100
Dark substitute	10	10	10	10	10	10
China clay (Devolite)	—	22·5	45	67·5	90	112·5
Stearic acid	0·75	0·75	0·75	1·0	1·0	1·0
Vulcafor VHM	5	5	5	5	5	5
Vulcafor VDC	0·75	0·75	0·75	0·75	0·75	0·75

CURE: 30 MINS. AT 141° C. PRESS CURE, FOLLOWED BY 2 HOURS IN AIR AT 125° C.

Tensile strength (kg./cm.^{2})	75	159	133	130	129	102
Elongation at break (%)	385	435	370	295	255	195
Modulus (kg./cm.^{2}):						
At 100% elongation	8	18	33	54	65	68
At 200% elongation	15	48	78	100	114	—
Hardness:						
Shore	40	50	58	64	68	90
B.S.I.	140	116	96	79	74	20
Resilience at 50° C. (%)	60	55	48	44	39	29

TABLE 247. SPREADING COMPOUNDS

Reference No.	J. 17444	J. 17445	J. 17446	J. 17447	J. 17448
Uses	Balloons and gas containers	Petrol diaphragms	Flexible petrol containers	Oil protective aprons	Cheap quality stock
Vulcaprene A	100	100	100	100	100
Nonox B.	2	2	2	2	2
Dark substitute	—	5	10	5	100
FT, MT or SRF carbon black	10	50	75	30	100
Channel black	—	—	—	15	—
Stearic acid	1·0	1·0	1·0	1·0	1·5
Added in Solution :					
Vulcafor VDM	10	10	10	10	10
Vulcafor VBN	0·75	0·75	0·75	0·75	0·75

CURE: 2 HOURS AT 125° C. IN AIR.

Permeability to gases (1/m.²/24 hrs. per 100 gm./m.²):					
Hydrogen	0·5	—	—	—	—
Nitrogen	0·07	—	—	—	—
Carbon dioxide	0·1	—	—	—	—
Oxygen	0·19	—	—	—	—
Ply adhesion	Balloon fabric breaks before plies separate				
Physical Properties of Unsupported Films from above Mixes :					
Modulus at 100% (kg./cm.²)	15	45	61	55	—
Freezing-point (R.A.E. test)	-50° C.	-50° C.	-50° C.	-50° C.	—

Permeability to petrol is one-sixtieth of neoprene GN.

TABLE 248. SOLVENT, OIL AND CHEMICAL RESISTANCE OF A TECHNICAL MIXING

SWELLING IN SOLVENTS (at 25° C.)	% Volume Increase			
	2 days	7 days	1 month	2 months
Petrol (F.75)	—	5	—	—
Benzene	75	80	80	80
Toluene	43	50	51	52
Xylene	18	30	37	38
Tetralin	8	14	32	40
Petroleum ether (40°–60° C.)	1·7	4·9	5·3	5·8
Carbon tetrachloride	15	20	41	41
Acetone	135	132	125	130
Methanol	42	38	39	40
White spirit	2·1	2·5	3·8	4·0
Paraffin	1·5	1·7	2·0	2·2
Cyclohexane	5·0	8·7	18	23
Decalin	1·2	2·1	3·3	4·5
Chloroform	411	420	—	—
Trichlorethylene	116	117	120	126
Ethanol	41	46	45	43
Water	4·5	7	9	10

SWELLING IN OILS 7 *days at* 70° *C.*	% Volume increase
Lubricating oil (D.T.D. 44D)	Nil
Diesel oil	Nil
Transformer oil	Nil
Linseed oil	Nil
Rosin oil	6
Castor oil	Nil

CHEMICAL RESISTANCE	
Water at 25° C.	In good condition after 3 months' immersion
Steam	Seriously attacked after 24 hours
5% caustic soda	Poor
5% hydrochloric acid	Poor
Ozone	Outstandingly good

REFERENCES

[1] BIGGS, ERICKSON and FULLER, *Ind. Eng. Chem.*, 1947, **39**, 1090.
[2] Dow Company, Technical Literature.
[3] DREYFUS, F.P. 462,274/1912.
[4] Hercules Powder Co., Technical Literature.
[5] LEUCHS, German P. 322,586/1920.
[6] LILIENFELD, B.P. 12,854/1912.
[7] WIGGAM, *Modern Plastics*, 1942, **19**, 51.
[8] Imperial Chemical Industries, Ltd.—Technical Literature.

CHAPTER 22

SOME ADDITIONAL COMPARATIVE PROPERTIES OF ELASTICS

IT is obviously a matter of great practical importance to be able to compare the properties of the various synthetic elastics, and also to be able to detect which type is present in any particular product.

Although these are still early days for any really comprehensive assessment and comparison of the merits of the various synthetic elastic materials, yet a certain amount of data has been accumulated.

The analytical side is very different. At the present time no scheme has been developed for the systematic examination and identification of the numerous existing materials and their compositions. The matter is complicated by lack of methods for identifying the various products.

There are, of course, many points of difference. A number of raw materials have some outstanding characteristics which facilitate recognition. For example, thioplasts can generally be readily detected by the typical unpleasant odour, which compounding cannot entirely eliminate. On the other hand, it is also the case that thioplasts are extensively used as modifying agents together with other synthetic elastics, so that a false conclusion could easily be reached.

Obviously the appearance of thermoplastic properties with rise of temperature sharply divides the groups of materials. But the identification of commercial highly compounded products is a very difficult proposition.

When one considers the complications of standard rubber analysis, the enormity of the task of establishing any systematic routine for the testing of highly compounded elastomers becomes apparent. Most commercial products are likely to contain high proportions of carbon black, which further complicates the problem. Furthermore, it must be remembered that no method exists for the direct estimation of natural rubber in a compound, this value invariably being obtained by difference. Consequently, the analytical aspect of synthetic elastics is beset with thorny problems.

Synthetic materials have some fairly obvious chemical differences from natural rubber, thus neoprene contains chlorine which could be readily detected analytically. Perbunan, too, contains a fairly large proportion of nitrogen which might be detected. But by far the most extensively used synthetic rubber is GR-S or Buna-S. This is a

pure hydrocarbon just like rubber, and behaves very much like it. Analysis will not show up any marked difference.

Comparative Properties of the Pure Materials. There is not a great deal of difficulty in differentiating between the various raw materials. Since they are not used in this condition these comparisons are clearly academic. Nevertheless, aids to identification are useful for routine purposes.

Appearance and odour will distinguish many. The only difficulty might be encountered in the elastomer group comprising the butadiene-styrene rubbers and the butadiene-acrylonitrile rubbers. The latter contains large proportions of nitrogen which can be estimated by the standard Kjehldahl method.

In the case of the thioplasts, apart from their odour, hydrogen sulphide will be emitted when they are subjected to the action of heat. The amount of free and bound sulphur can be estimated by the usual technique employed for vulcanized rubber.

The action of heat on neoprene, polyvinyl chloride, and polyvinylidene chloride will cause evolution of gases which will give the typical cloudiness in silver nitrate solutions showing the presence of chlorine. The polyacrylic esters give characteristic odours of the monomers when strongly heated.

Comparison of Physical Properties. Many interesting differ-

TABLE 249. DENSITIES OF UNVULCANIZED MATERIALS

Material	Density gm./c.c.
Natural rubber	0·911
Neoprene	1·25
Perbunan	0·96
Perbunan-Extra	0·97
GR-S	0·9
Hycar O.R.	1·00
Chemigum	1·06
Thiokol RD	1·03
Butyl rubber	0·91
Thiokol A	1·60
Thiokol DX	1·34
Thiokol F	1·38
Perduren G	1·68
Perduren H	1·56
Perduren L	1·17
Vistanex H.M. (25° C.)	0·9125
Vinyl chloride polymer 0% plasticizer	1·42
Vinyl chloride polymer 30% ,,	1·33
Vinyl chloride polymer 60% ,,	1·25
Polyvinyl formal	1·23
Polyvinyl butyral	1·110
Polyacrylic ester	1·200

ences are shown up by comparisons of various physical properties. Thus the densities are shown in Table 249. The straight hydrocarbon materials have the lowest densities, while the materials containing high proportions of chlorine and those containing sulphur are the heaviest materials.

Wood[17] has determined the densities of a number of available synthetic elastics very carefully. His results are shown in the following table:

TABLE 250. DENSITY VALUES AT 25° C.

Name	Manufacturer	Density gm./c.c.
Neoprene GG.	Du Pont Co.	1·2307
Neoprene E	Du Pont Co.	1·2384
Neoprene FR	Du Pont Co.	1·1406
Neoprene GN	Du Pont Co.	1·2290
GR-S	Firestone Tyre & Rubber Co.	0·9291
GR-S	Firestone Tyre & Rubber Co.	0·9358
GR-S	U.S. Rubber Co.	0·9369
GR-S	Standard Oil Development Co.	0·9390
Chemigum IV	Goodyear Tyre & Rubber Co.	0·9391
Hycar OS-20	B. F. Goodrich Co.	0·9385
Hycar OS-30	B. F. Goodrich Co.	0·9303
Chemigum I	Goodyear Tyre & Rubber Co.	1·0135
Hycar OR	B. F. Goodrich Co.	0·9992
Perbunan	Standard Oil Development Co.	0·9684
Thiokol RD	Thiokol Corp.	1·0564
Thiokol A	Thiokol Corp.	1·5983
Thiokol FA	Thiokol Corp.	1·3298
Butyl B-1·45	Standard Oil Development Co.	0·9175

Many of the thermoplastic materials, the ethenoid resins in particular, are valued because of their transparency. Polyvinyl butyral depends entirely on the combination of transparency with rubber-like properties. In this connection the refractive indices of the various materials is of some interest.

TABLE 251. REFRACTIVE INDICES OF UNVULCANIZED MATERIALS

Material	Temperature ° C.	n_D
Natural rubber	25	1·5190
Neoprene	25	1·5580
Neoprene	30	1·5562
Perbunan	25	1·5213
Perbunan	30	1·5562
Vistanex H.M.	25	1·5089
Vistanex L.M.	10	1·5131
Components of plasticized vinyl chloride polymers:—		
Vinyl chloride polymer (unplasticized)	40	1·565
Tricresyl phosphate (plasticizer)	40	1·5494
Polyacrylic ester	20	1·49
Polyvinyl butyral	26	1·488
Polyvinyl formal	20	1·50

Examination of these materials under ultra-violet light does show up certain distinctive features. The behaviour is shown in the following table:

TABLE 252. EFFECT PRODUCED BY ULTRA-VIOLET LIGHT

Material	Colour by Ultra-violet Light
Butadiene polymers and Copolymers	Strong violet
Polyvinyl formal	Strong whitish-blue
Polyacrylic ester	Bright blue with red tint
Polyvinyl chloride	Greenish blue
Polyacrylic nitrile	Light yellow
Polyvinyl alcohol	Bright white
Neoprene GN	Blue white on fresh surface
Neoprene I	Dull blue
Thiokol A	No fluorescence; dark brown colour
Thiokol B	" " " " "
Thiokol F	Dark purple
Thiokol FA	Pale white fluorescence
Thiokol RD	Brilliant blue-white
Novoplas A	No fluorescence
Polyisobutylene	Light blue

The period length of fibre patterns obtained by X-ray examination of stretched samples supplies another set of values which is of interest from an academic angle as contributing towards a knowledge of the structure of the materials concerned.

TABLE 253. X-RAY DIAGRAM: STRETCHED RUBBER-LIKE SUBSTANCES

Material	Fibre Period in Å after Stretching the Sample
Polyvinyl alcohol [7]	2·52
Thiokol A [5]	4·32
Polyvinylidene chloride [2]	4·71
Neoprene [3]	4·8
Gutta-percha	4·8
Polyvinyl chloride [5]	5·0
Rubber [9]	8·2
Thiokol B	8·8
Polyisobutylene [6]	18·5

Analytical Methods. Identification and estimation of synthetic rubbers in their vulcanized compounds has become a thorny problem. Satisfactory methods are absolutely essential. Ordinary analytical methods have not proved particularly suitable. However, effective new methods are beginning to emerge. New materials call for new techniques and these are being developed as time goes by.

Barnes, Williams, Davis and Giesecke [1] have described two successful methods which show promise. The first method is based upon the

phosphorus content. It is an interesting example of the close study of details. It is based upon the observed fact that the metabolic processes of plants bring about in the plant the deposition of a great many of the metals commonly found in the soil. By contrast with this, the metals found in any synthetic product are limited to those purposely added and those accidentally introduced.

The phosphorus contents of a variety of natural and synthetic rubbers are given in Table 254. These values show a considerable variation for natural rubbers of different origins, but all may be characterized by high phosphorus (average 400 parts per million) when compared with typical synthetics (average 20 parts per million). Thus, an exact phosphorus determination should make possible a determination of the ratio of natural to synthetic rubber in an unknown sample.

Phosphorus can be determined accurately enough to allow the content of this element to be used as a yardstick and as a direct measure of the amount of natural rubber present.

TABLE 254. PHOSPHORUS CONTENT OF VARIOUS RUBBERS

	P.p.m.		P.p.m.
Natural Rubber—		*Synthetic Rubber—*	
Smoked sheet A	690	Buna-S (American)	15
Smoked sheet B	380	Buna-A (German)	30
Smoked sheet C	320	Cotton tyre cord	210
Smoked sheet D	500	Viscose tyre cord	10
Smoked sheet E	400		
Crepe	490		
Pale crepe	350		
Reclaimed tube	390		
Guayule	200		

In spite of the variation of the phosphorus content of natural rubbers of different origin, a reasonable first guess at a mixture of unknown constitution may be based on the following generalization:

High phosphorus	(300 to 450 p.p.m.)	= natural
Medium ,,	(100 to 250 p.p.m.)	= natural + synthetic
Low ,,	(0 to 50 p.p.m.)	= all synthetic

As will be seen from Table 254, the above method provides a very simple approximate analysis. There is good agreement between this method and other methods. However, the method is always open to the uncertainty that phosphorus may have been introduced in processing.

Obviously all equipment and reagents must be free of phosphorus. Fabrics, cords, etc., are a possible source of phosphorus and also phosphorus-containing plasticizers. All these must be removed. An

additional feature of interest was that they found that natural fibres (cotton, etc.) are high in phosphorus, whereas synthetic fibres, rayons, etc., are low. These are removed by digesting the sample in excess cuprammonium solution. Plasticizers containing phosphorus are removed by refluxing shredded samples for 8 hours in chloroform and acetone.

The weighed sample of extracted rubber is ashed in a suitable crucible in a controlled furnace at a temperature not higher than 600° C. until free of organic material. After cooling, the residue is dissolved by boiling in just sufficient dilute sulphuric acid to dissolve the soluble materials.

Colour is developed by additions of standard solutions of ammonium molybdate, dilute sulphuric acid and stannous chloride. The conditions are all rigorously standardized.

The percentage transmission of the solution in a 1-cm. thick cell at 700 mμ is measured exactly 20 minutes after adding the stannous chloride. The amount of phosphorus in an unknown compound may be determined from a calibration curve which shows the percentage transmission plotted against the phosphorus content of known standard solutions.

Infra-Red Spectroscopy. There has been a great deal of interest in applications of infra-red spectroscopy to the identification and analysis of many types of organic materials. Barnes, Williams, Davis and Giesecke pointed out the two salient characteristics of infra-red absorption which form the basis for analysis.

The infra-red absorption spectrum is the curve of percentage transmission against the frequency. It is a unique characteristic of the material and cannot be duplicated by another compound. Some of the absorption bands can be ascribed to particular atomic groups within the molecule ; others, characteristic of the molecule as a whole, are particularly useful for such studies as differentiating isomers. Thus it is to be expected that the phenyl group in Buna-S would give rise to absorption bands which would not be present in natural rubber, while conversely, the methyl groups of natural rubber would cause a characteristics absorption which would not be observed in Buna-S. Moreover, it is to be expected that there will be further bands characteristic of the molecule as a whole which will assist in the differentiation.

In the second place, so long as no intermolecular action occurs, the spectrum of a mixture of rubbers will be simply the spectra of the pure components combined in the proportion in which the materials themselves are present. Hence, it is to be expected that an unknown mixture can be analysed by direct measurement of the strength of

absorption bands unique to each component, or by comparison of the absorption spectra of the unknown with those of a series of known prepared standards.

The differences in the infra-red absorption spectra of various rubbers readily show their applicability in identifying an unknown rubber or in estimating the content of a mixture. They found that GR-S has a strong aromatic ring frequency near 1500 cm.$^{-1}$ and two strong bands at 970 cm.$^{-1}$ and 917 cm.$^{-1}$ which are not present in natural rubber. Natural rubber, on the other hand, shows a methyl band at 1380 cm.$^{-1}$ and a strong band at 835 cm.$^{-1}$ which are not observed in GR-S. Taking advantage of these differences, each unknown sample could be analysed by comparison of its spectrum with the spectra of a series of known mixtures. All absorption spectra were taken with samples smeared on Salt plates and a high-resolution spectrometer was employed. The accuracy of the method is limited to 5 to 10 per cent. because of the inability to make smear samples of constant thickness. Using the two methods described, Barnes, Williams, Davis and Giesecke examined some of the captured German tyres with the results shown in Table 255.

Kluckow [8] has described some of the criteria employed in Germany to distinguish between the many and varied types of synthetic elastics. He considered them in relation to natural rubber.

Natural rubber (sp. gr. 0·93, nitrogen content up to 4 per cent.) begins to soften above 120° C., at still higher temperatures turns into a thick brown oil, which with continued heating yields a large number of dissociation products with boiling points from 18° C. to 300° C. Natural rubber easily burns when held in a flame, giving off a great deal of thick smoke. Finely ground rubber swells and becomes jelly-like in benzene. When rubber is masticated on cold rolls for various periods, rubber solutions with rapidly decreasing viscosity result.

The butadiene-styrene copolymers Buna-S and Buna-SS (sp. gr. 0·92, nitrogen content 0·02 per cent. ; portion soluble in acetone, 6·2 to 6·9 in the case of Buna-S and 6·9 to 8·1 in the case of Buna-SS) burn with a thick smoky flame ; they also swell and become jelly-like in benzene when finely ground, but mastication has considerably less effect than on natural rubber.

Perbunan (butadiene-acrylic-nitrile copolymer) has a specific gravity of 0·92 ; while the nitrogen content is 6·7 to 7·3 per cent. ; unlike the other synthetic rubbers and natural rubber it is soluble in ketones (acetone) and, when burnt, gives off a more aromatic odour than natural rubber, which can easily be distinguishable from the odour of burning Buna-S or Buna-SS.

TABLE 255. ANALYSIS OF CAPTURED GERMAN TYRES

Tyre No.	Phosphorus (p p m)	Phosphorus Natural (%)	Infra-red Natural (%)	Infra-red Buna-S (%)
	TREAD STOCKS			
FT. 61	280	75	100	0
99	30	0	0	100
100	20	0	0	100
101	10	0	0	100
102	10	0	0	100
103	30	0	0	100
104	25	0	0	100
105	20	0	0	100
106	27	0	0	100
107	3	0	0	100
	CARCASS STOCKS			
FT. 61	340	100	100	0
99	340	100	100	0
100	380	100	100	0
101	430	100	100	0
102	130	25	20	80
103	190	50	50	50
104	230	60	50	50
105	200	50	80	20
106	305	80	100	0
107	190	50	50	50
	CUSHION AND TUBES			
FT. 61 [a]	290	75	100	0
99 [a]	270	70	100	0
101 [a]	450	100	—	—
102 [b]	200	50	75	25
103 [b]	255	65	75	25
104 [b]	285	70	85	15
105 [b]	295	75	100	0
106 [b]	260	70	100	0
107 [b]	290	75	100	0

[a] Cushion. [b] Tubes.

The chloroprene polymers, Neoprene or Sovprene (sp. gr. 1·25), have a characteristic odour. When heated to 50–60° C. they become softer and stickier than masticated rubber. They do not burn when held in a flame.

Perdurens (Thioplasts) have a peculiar, unpleasant odour; when samples are heated in a test tube, the smell is of sulphide of hydrogen

and other sulphur compounds, but when they are burnt, there is an acrid sulphur-dioxide odour. Perdurens are soluble in trichlorethane, but not in benzene and benzol. Sheets of the materials have a tendency to flow in storage.

The chemical characteristics of Thiokol are the same as of the Perdurens ; the specific gravity is 1·62, sulphur content about 83 per cent. It also is soluble in trichlorethane, but insoluble in benzene, benzol, and mixtures of motor oils.

Kluckow extended his comments about vulcanized materials as follows. Vulcanized natural rubber goods are most easily identified by burning, when the well-known burnt rubber odour should be detectable. Another means of identification is testing the extensibility. Buna and Perbunan goods do not give off a rubber odour when burnt. Benzene hardly affects Perbunan goods, but its action on Buna-S and Buna-SS is distinctly noticeable.

Light-coloured Buna and Perbunan vulcanizates and those low in fillers have poorer elasticity and tensile values than natural rubber vulcanizates. The tensile strength of the synthetic rubbers only approaches that of natural rubber when carbon black is present in appreciable quantity.

According to Kluckow, Thiokol and Perduren goods give an acrid sulphur dioxide odour emitted when they are burnt, and are easily recognized. The high sulphur content is also responsible for the high specific gravity. Although very resistant to oils and fats, their mechanical properties are comparatively poor. Furthermore, they have relatively low resistance to heat, and, as a result of the high sulphur content, harden more rapidly around 100° C. than other materials.

Neoprene goods can be distinguished by the fact that in consequence of the high chlorine content, they do not burn when held in a flame ; they resist benzene, petroleum, and mineral oils, but swell rapidly in benzol and chlorinated hydrocarbons. Unlike Perduren and Thiokol, they resist heat well and have better mechanical properties.

Non-vulcanizable synthetics are usually employed in combination with softeners, resins, fats, etc., and when so compounded, it is almost impossible to distinguish them. However, when used alone or mixed with inorganic fillers only, the odour when they are burnt is a serviceable guide.

Softened polyvinyl chlorides (Igelites), says Kluckow, compounded or not, give off a strong hydrochloric odour when burnt. Their cold resistance is lower than that of the vulcanizates, and compared with neoprene vulcanizates, they also have less resistance to heat. For

whereas the latter remain hard at temperatures of 140–170° C., Igelites soften under these conditions.

Polymerized isobutylene compounds (Oppanols) easily dissolve in benzene. They retain their flexibility at extremely low temperature.

Oppanols and polyacrylic acid esters yield ester-like, odiferous dissociation products when subjected to dry distillation.

Colour Reactions for Synthetic Rubbers. Burchfield [3] has described a new colour reaction which serves to characterize natural rubber, GR-S, and Perbunan. Confirmatory tests included in the same operation distinguish between the remaining commercially important types. The procedure is sufficiently rapid to be practical in the testing of representative samples.

Spot tests are proposed which are carried out by holding impregnated filter paper strips in the smoke emitted when the sample is branded with a metal rod heated to redness. Colour changes take place which indicate the nature of the polymer. One test distinguishes between natural rubber and GR-S, a second is specific for Butyl, while a third differentiates Neoprene GN, Neoprene ILS, and Perbunan from one another and from the hydrocarbon rubbers. The spot reactions can be carried out very rapidly.

Reactions can be carried out more conveniently on the pyrolyzates than on the original materials. Although GR-S contains aromatic nuclei, and natural rubber is purely aliphatic, this distinction does not apply to their pyrolyzates, for which the primary decomposition products of rubber are isoprene and dipentene, a number of aromatics are produced through secondary reactions. Definite distinction can be made by reacting the pyrolyzates with materials capable of condensing with compounds containing labile hydrogen atoms. *p*-Dimethylaminobenzaldehyde was found to yield coloured condensation products with the distillates from a number of polymers, which are sufficiently characteristic to serve as criteria of identity.

The pyrolyzate from a rubber sample is distilled into a dilute alcoholic hydrochloric acid solution of the aldehyde. An initial colour is produced which is intensified and altered by diluting the reaction mixture with methanol and heating on a water bath. The distillate from natural rubber produces an intense violet-blue, and that from GR-S a green. Perbunan yields a red product, neoprene a yellow-green, and Butyl a blue-green of comparatively low intensity.

Solution I. Dissolve 1·0 gram of *p*-dimethylaminobenzaldehyde and 0·01 gram of hydroquinone in 100 ml. of absolute methanol. Add 5 ml. of concentrated hydrochloric acid and 10 ml. of ethylene glycol. The specific gravity is adjusted to 0·851 with ethylene glycol, so that

butyl rubber can be distinguished from the other polymers by the low density of its pyrolysis product. The reagent is stable over a period of several months when stored in a brown bottle.

Solution II. Dissolve 2·00 grams of sodium citrate, 0·20 gram of citric acid, 0·03 gram of bromocresol green, and 0·03 gram of Metanil yellow in 500 ml. of distilled water. The initial colour is green, which changes to yellow in the presence of acetic acid and to red in the presence of hydrochloric acid. These colour changes are used for distinguishing polymers which yield organic acids and those which contain chlorine, from one another, and from materials which give neutral or alkaline products or decomposition.

Ten 75-mm. soft glass test-tubes heated with a microburner are employed. The tubes are inexpensive and can be discarded after one use. A small sample is required, which is often of importance in the analysis of surface coatings or other materials which are available only in small quantities.

TABLE 256. PYROLYSIS TESTS

	Solution I		Solution II
Material	Initial Colour	Colour after heating	Colour
Blank	Pale yellow	Pale yellow	Green
Polyvinyl chloride	Yellow	Yellow	Red
Neoprene GN	Yellow	Pale yellow-green	Red
Neoprene ILS-neoprene-Perbunan mixtures	Orange red	Red	Yellow to red
Perbunan	Orange red	Red	Green
GR-S	Yellow-green	Green	Green
50 GR-S-50 rubber	Olive green	Green-blue	Green
Natural rubber	Brown	Violet-blue	Green
Butyl	Yellow (droplet floats)	Pale blue-green	Green
Polyvinyl acetate	Yellow	Pale yellow-green	Yellow

Table 256 describes the reactions which occur when the decomposition products from the compounded polymers are distilled into the test solutions. In the case of the aldehyde reaction, both the initial colour and that obtained after dilution and heating are listed. The table includes the types in most common use, and two simple mixtures, in which both components are present in considerable amounts.

Procedure. Place approximately 0·5 gram of the sample in a 10 × 75 mm. test-tube and attach a 4-mm. outside diameter side-arm by means of a cork. Suspend the tube by a wire from a ring stand and heat with a microburner until the sample begins to decompose. Avoid localized overheating to prevent softening of the glass.

When vapours appear at the mouth of the side-arm, immerse the end beneath the surface of 1·5 ml. of solution II contained in a 10 × 75 mm. tube. After it is evident whether a colour change will take place or not, remove the tube and continue the distillation into 1·5 ml. of solution I. Permit the tubes to cool for a minute or two and shake. Note the position of the droplet in solution I and the colour changes which take place. Transfer solution I to a 16 × 150 mm. test-tube and add 5 ml. of absolute methanol. Heat on a water-bath at 100° C. for 3 minutes and note the colour which develops. A description of the reactions obtained is given in Table 256.

If the absence of other interfering polymers has been established by the above test and the principal interest lies in the detection of natural rubber and GR-S, repeat the experiment on a 0·2- to 0·3-gram chloroform-extracted sample. Collect the total distillate under the 1·5 ml. of solution I and note the colour of the solution before and after heating. If a blue-green to green-blue colour is obtained, it is probable that the sample is a rubber–GR-S mixture or a natural rubber reclaim. Test for the presence of crude rubber by the Weber method, and if necessary confirm the presence of GR-S by the coupling procedure.

Absorption curves of the reaction products of the pyrolysates obtained from vulcanized chloroform-extracted samples show marked differences and are characteristic of the respective materials.

Spot Tests. When large numbers of samples must be tested, Burchfield has evolved the use of convenient spot methods. The general procedure is to dip a prepared indicator paper into a wetting solution and hold it in the smoke which is emitted when the sample is branded with a metal rod heated to redness. A characteristic colour reaction is obtained in 4 to 6 seconds.

For the detection of neoprene and Perbunan, the papers are impregnated with Metanil yellow and cupric acetate and dipped in an alcoholic solution of benzidine dihydrochloride prior to use. If the polymer contains chlorine, a red colour is produced by the action of the liberated hydrochloric acid on the acid-base indicator. This will ordinarily serve as a test for neoprene or polyvinyl chloride, although other chlorine-containing polymers give similar results. If the sample is Perbunan or a polymer containing nitrile nitrogen, a green colour appears, due to the presence of cyanide radicals in the decomposition products. This reaction, which takes place in the presence of benzidine and copper acetate, has been widely used for the detection of hydrocyanic acid in air. The colour is normally blue but is modified to a green by the colour of the acid-base indicator. If substantial amounts of both chlorine and nitrile nitrogen are present as in Neoprene ILS,

and neoprene-Perbunan mixtures, both colours appear in bands on the filter-paper strip, the green colour appearing on the wet zone, and the red colour most prominently on the dry portion of the paper. In the presence of the hydrocarbon rubbers no colour changes are observed, although the paper may darken on drying. The presence of GR-S or natural rubber in admixture with either of these types does not alter the results obtained by the test, but the appearance of the colours may be delayed by dilution of the active constituents.

Butyl rubber is distinguished from natural rubber and GR-S by the use of blank filter-paper strips which are immersed in a solution of mercuric sulphate in dilute sulphuric acid prior to making the tests. The pyrolysate obtained from butyl yields a brilliant yellow colour, while rubber and GR-S produce dull browns. The test depends on the presence of isobutylene in the decomposition products, which reacts with mercuric sulphate to form a complex with empirical formula corresponding to $C_4H_8(HgSO_4.HgO)_3$.

The most useful test in the series is that which distinguishes natural rubber from GR-S. The materials required are prepared indicator paper strips impregnated with *p*-dimethylaminobenzaldehyde, and a 30 per cent. solution of trichloroacetic acid in isopropanol. A strip of indicator paper is dipped in the acid solution and held in the smoke emitted when a hot rod is held against the surface of the polymer. Rubber produces an intense blue coloration and GR-S a green. Mixtures containing equal parts of the two substances test as GR-S, although the green may be modified to a blue-green. Samples containing 25 parts and less of GR-S test as natural rubber. The principle difficulty is caused by indecision in the classification of mixtures. The test is of value only for distinguishing GR-S from natural rubber, as the other polymers also give colour reactions. While by careful observation it is possible to distinguish some of the other types, more specific tests are preferred. Butyl produces a blackish coloration which fades to a pale lavender on standing 3 to 4 minutes. Perbunan produces a green colour, but if the paper is held close to the heating unit until dry, a reddish-brown spot appears. Neoprene gives a reaction almost indistinguishable from that of GR-S. Although the reaction is not specific, it may be used without supporting tests in many instances where it is only necessary to distinguish between natural rubber and GR-S.

A summary of the reactions obtainable by use of the spot tests is shown in Table 257.

Apparatus. The tests can be conveniently carried out by use of a triangular file heated to redness in a Bunsen flame.

TABLE 257. SPOT TESTS

	Neoprene Perbunan test	Butyl test	Rubber-GR-S test
Neoprene GN	Red	—	—
Perbunan	Green	—	—
Neoprene ILS, neoprene-Perbunan mixtures	Red/Green	—	—
Butyl	Blank	Yellow	—
Natural rubber	Blank	Brown	Blue
GR-S	Blank	Brown	Green

Indicator Papers and Reagents. *Neoprene-Perbunan Test.* Dissolve 2·0 grams of cupric acetate and 0·25 gram of Metanil yellow in 500 ml. of methanol. Impregnate filter-paper squares with the solution, dry, and cut into strips. Dissolve 2·5 grams of benzidine dihydrochloride in a mixture of 500 ml. of methanol and 500 ml. of water. Add 10 ml. of a 0·1 per cent. aqueous solution of hydroquinone. Store in a brown bottle. A precipitate forms on standing, but if the solution is protected from light and air, it can be used for several months.

Butyl Test. Use blank filter-paper strips. To prepare the wetting solution, add 5·0 grams of yellow mercuric oxide to a mixture of 15 ml. of concentrated sulphuric acid and 80 ml. of water. Bring to a boil and continue heating until the oxide dissolves. Cool and make the volume up to 100 ml. with water.

Rubber–GR-S Test. Impregnate filter-paper squares with a solution of 3 grams of *p*-dimethylaminobenzaldehyde and 0·05 gram of hydroquinone in 100 ml. of ethyl ether. Dry and cut into strips. Papers stored in brown glass bottles show no discoloration and retain their activity after several weeks' storage. On prolonged storage under adverse conditions, the aldehyde oxidizes and the tests become progressively less distinct. To prepare the wetting solution, dissolve 30 grams of trichloroacetic in isopropanol and make the volume up to 100 ml. This solution must be used with care.

Procedure. Wet a 1-cm. section of the test-paper with the corresponding impregnating solution and hold it in a parallel position about 5 mm. from the surface of the heating element which is pressed against the rubber sample. If the evolution of vapour is sufficiently rapid, an adequate test is obtained in 4 to 6 seconds. In testing for natural rubber and GR-S, it is desirable to continue the test until the colour which is formed can be seen through the back of the paper. The hue should be judged from the appearance of the paper facing the heating element. Charring the paper and overdeveloping the colour should be avoided.

The reactions which are obtained from the various polymers, using the three types of indicator papers, are summarized in Table 257.

Detection of Mixtures. A general procedure for the detection of mixtures requires more specific and detailed methods than those described. However, by careful observation of the results obtained by the pyrolysis procedure, it is frequently possible to detect deviations from normal behaviour which will indicate the need for a more complete analysis.

Compounds containing natural rubber and GR-S present in approximately equal amounts yield green-blue reaction products which are readily distinguishable from those of the pure materials. The test is not applicable to compounds in which the minor constituent comprises less than 25 to 35 per cent. of the total polymer, as the colours are difficult to match and may be simulated by the presence of other materials. Natural rubber reclaims produce green-blue to blue colours which differ in appearance from those obtained on compounds based on crude rubber and may suggest the presence of GR-S as the minor constituents of a mixture. In such cases more specific tests must be applied to make identification certain.

Experiments on samples of known composition indicate that the Weber test can be used to detect natural rubber in the presence of GR-S, neoprene, and Perbunan. Positive reactions are obtained from natural rubber (Hevea), guayule, and balata. A violet colour of low intensity is obtained on testing polyvinyl acetate. Natural rubber reclaim gives a red-violet colour which is distinguishable from the opaque blue-violet obtained on testing samples containing crude rubber.

A qualitative test for GR-S in the presence of natural rubber is described by British investigators. The extracted sample is nitrated, reduced, and diazotized. The formation of a crimson azo dyestuff on coupling with β-naphthol indicates the presence of GR-S, or more generally, the presence of a polymer containing aromatic groups. The method is of value whenever a laboratory procedure can be used and serves to establish the presence of GR-S in small amounts.

Perbunan is readily detected in the presence of neoprene by the reaction with p-dimethylaminobenzaldehyde, as the intense red colour masks the yellow-green of the neoprene. On testing Neoprene ILS, which contains both nitrile nitrogen and chlorine, positive tests for both groups are obtained in the initial pyrolysis procedure. The acid-base indicator confirms the presence of an acidic material in the decomposition products, while the aldehyde reaction indicates the presence of a nitrogenous polymer. Perbunan can also be satisfactorily

detected in mixtures by the copper acetate-benzidine reaction or by the Prussian-blue test.

The presence of neoprene as a minor constituent in mixtures is established by use of the Beilstein test when the low concentration and the presence of alkaline compounding ingredients obscure the normal acid reaction.

A copper wire is heated to redness and touched to the sample. If, on reheating, a brilliant green colour is imparted to the flame, a compound containing chlorine is present. Polyvinyl chloride and other non-vulcanizable polymers can be distinguished from neoprene by extracting the sample with acetone and examining the residue obtained on evaporating the solvent for the presence of a resinous material of high chlorine content. Neoprene is not removed from vulcanized compounds by acetone extraction. This procedure is of general value for distinguishing curing from non-curing polymers when present in mixtures. The choice of the solvent and the method of isolating the extractable polymer from the residue must be decided in each case from a knowledge of the properties of both constituents.

Comparison of Properties of Vulcanized Materials and Compounded Materials. In 1940 Wood[18] prepared an excellent summary of existing information on synthetic elastics. Some of his tables have been modified and extended in the light of subsequent experience. For example, it is of considerable practical interest to be able to compare the tensile strength and elongation of synthetic elastic with the values for natural rubber. While the compounds are not strictly comparable, the figures do afford some guide in this respect. The individual characteristics in relation to fillers, etc., have already been commented upon.

Table 259 gives a useful summary of characteristics of various synthetic materials with emphasis on factors of interest from the engineering viewpoint.

The excellent swelling characteristics of most synthetic elastics in contact with solvents and oils are largely responsible for their existence, and certainly constitute the chief justification for the high cost.

Another useful comparison is given by the resistance offered to many corrosive chemicals and solvents. There is little quantitative data on this aspect and only a qualitative indication can be offered.

Solubilities of Unvulcanized Rubbers. Sarbach and Garvey[14] have made very extensive solubility studies on unvulcanized rubbers. These are very useful both to indicate the type of materials most likely to be good solvents and softeners and to indicate the effect of various solvents and oils on the vulcanized rubbers.

TABLE 258. MAXIMUM TENSILE STRENGTHS AND CORRESPONDING ELONGATIONS

	Unvulcanized		Vulcanized pure gum		Vulcanized carbon black compound	
	T_B kg/cm²	E_B %	T_B kg/cm²	E_B %	T_B kg/cm²	E_B %
Natural rubber[13]	25	1200	290	710	350	650
Neoprene[9]	30	1100	300	820	290	760
Buna 85	—	—	—	—	175	600
Buna 115	—	—	—	—	200	700
Buna-S	—	—	—	—	280	650
Perbunan	—	—	150	900	320	600
Hycar OR	—	—	48	540	300	510
Butyl rubber	—	—	250	1000	—	—
Thiokol " A "	—	—	—	—	60	370
Thiokol " D "	7	570	35	750	120	610
Thiokol " RD "	-	—	—	—	220	530
Vistanex M.M.	20	1000	Not vulcanizable		Not vulcanizable	
Vistanex H.M.	60	1000	"	"	"	"
Koroseal 0% plasticizer	400	2	"	"	"	"
Koroseal 30% plasticizer	270	170	"	"	"	"
Koroseal 60% plasticizer	70	500	"	"	"	"
Polyvinyl chloride 50% Tricresyl phosphate	160	350	"	"	"	"
Vinylite V. 33% plasticizer	210	300	"	"	"	"
Polyvinyl formal	250	100	"	"	"	"
Polyvinyl butyral	175	400	"	"	"	"
Acrylic ester (66% carbon black)	50	250	"	"	"	"

By investigating the effect of a wide variety of solvents on a single rubber they showed that it is possible to tell which groups have good solvent action and which do not. This information makes it possible to predict, with considerable accuracy, the solvent power of any material of known composition. The solvent power of a given material together with chemical stability, boiling-point, melting-point, and viscosity, indicates quite well its utility as a softener. In many cases the nature of the solution also indicates whether or not the material will be an effective tackifier. Usefulness of such solubility data in cement manufacture is obvious.

It is generally true that materials which are good solvents for an unvulcanized rubber are strong swelling agents for the same rubber when vulcanized. Here also such properties as melting-point and

TABLE 259. PHYSICAL PROPERTIES OF SYNTHETIC AND NATURAL RUBBER [13]

	S.G.	T.S.	Shore hardness	Max. temp. use	Dielectric strength v./mm.
Buna-S	0·94	3800	15/90	300	—
Butyl	0·91	500–3000	15/90	250/300	25,000
Chemigum—Oil Res.	1·0 –1·5	800–4000	30/90	300	—
Chemigum-tyres	1·0 –1·15	1000/4000	50/65	450	—
Hycar OS, hard	1·1 –1·3	4000/11,000	—	300	—
Hycar OR, soft	0·99–1·6	1000/4500	15/95	300	—
Hycar OS, soft	0·96–1·20	1000/4000	20/95	250	—
Koroseal,[a] hard	1·3 –1·4	2000/9000	80/100	212	30,000/50,000
Koroseal, soft	1·2 –1·3	500/2500	30/80	190	15,000/30,000
Neoprene	1·25–1·30	1000/4500	15/95	300	—
Perbunan	0·96	500/5000	30/90	300	—
Resistoflex [b]	1·26	2000/5000	—	250	6000/10,000
Thiokol FA	1·34	1400	25/90	200	—
Vistanex,[c] medium	0·9	200	—	—	—
Vistanex, hard	0·9	550	—	—	—
Natural rubber, hard	1·17–1·18	4000/11,000	70/100	220	—
Natural rubber, soft	0·93–1·17	1000/6000	30/80	150/180	—

	Heat effect	Abrasion resistance	Sunlight effect	Ageing effect	Machining qualities
Buna-S	Stiffens	= to rubber	Slight	= rubber	Can be ground
Butyl	Softens sl.	Good	None	Better than rubber	Can be ground
Chemigum—Oil Res.	Stiff.	Excellent	= to rubber	Stiffens	Can be ground
Chemigum-tyres	Stiff	Excellent	Deteriorates	None	—
Hycar OS, hard	Softens 300	Good	V. slight	None	Excellent
Hycar OR, soft	Stiff. sl.	Excellent	Slight	Highly resistant	Can be ground
Hycar OS, soft	Stiff. sl.	Excellent	Slight	Highly resistant	Can be ground
Koroseal,[a] hard	Softens	Good	None	None	Good
Koroseal, soft	Softens	Good	None	None	Can be ground
Neoprene	Softens sl.	Excellent	None	Highly resistant	Can be ground
Perbunan	Softens sl.	Excellent	Slight	Highly resistant	Can be ground
Resistoflex [b]	Softens	Good	None	None	—
Thiokol FA	Hardens sl.	F.G.	None	None	Excellent
Vistanex,[c] medium	—	—	None	Better than rubber	Cannot be machined
Vistanex, hard	—	—	None	Better than rubber	Cannot be machined
Natural rubber, hard	Softens	Good	Discolours	None	Excellent
Natural rubber, soft	Softens and deforms	Excellent	Deteriorates	Highly resistant	Can be ground

[a] Polyvinyl chloride. [b] Polyvinyl alcohol. [c] Polyisobutylene.

TABLE 260. SWELLING OF VULCANIZED COMPOUNDS IN LIQUIDS [11]

Volume increase, in percentage, after immersion for 8 weeks at room temperature

	Natural rubber	Neoprene	Perbunan	Perbunan-Extra	"Thiokol" A	"Thiokol" D	"Thiokol" DX and F
Light gasoline (Benzine)	160	—	20	20	0	—	—
Gasoline	230	8	40	—	0	3	3
Kerosene	—	60	—	—	0	2	2
Diesel oil	120	—	15	15	—	—	—
Fuel oil	—	—	—	—	0	10	10
Lubricating oil	—	40	−4	—	0	1	1
Paraffin oil	140	—	3	—	—	—	—
Transformer oil	150	—	5	—	—	—	—
Acetone	—	25	110	110	—	—	9
Benzene	370	160	270	140	7	150	90
Carbon tetrachloride	670	160	220	120	0	40	30
Ethyl ether	130	50	50	—	—	—	—
Linseed oil	100	—	20	—	—	1	1
Turpentine	300	90	50	30	0	—	—

viscosity have an important bearing on the time required to reach equilibrium and the permanence of the swelling action.

Procedure. The elastomers were masticated on a warm mill until broken down. The $\frac{1}{32}$-inch rubber sheets were then rolled into parchment directly off the mill. The plasticized polyvinyl chloride (Koroseal sheet, 59 per cent. P.V.C., 41 per cent. tricresyl phosphate) used in this study was compounded, milled, and moulded into $\frac{1}{32}$-inch sheets. Approximately 20 c.c. of the solvents were placed into small vials, and 0·5 gram of the freshly prepared elastomer was added. All vials were kept at room temperature except those containing phenol, tertiary butyl catechol, and ethyl pentachlorobenzene. These were kept at Temperatures above their melting-points. Observations were made after two and four hours, and one, five and seven days. The vials were thoroughly stirred before each inspection. Their results are shown in Table 261.

Interpretation of Results. In using these solubility data in finding the answers to practical questions which frequently arise in rubber practice, it should be realized that the study was made on pure gum unvulcanized elastomers and that application of the data to vulcanizates necessitates the use of considerable discretion on the part of the interpreter. A solvent which quickly dissolves a pure gum unvulcanized rubber will naturally not dissolve a compounded vulcanizate, but tests have shown it to be generally true that a solvent which quickly dissolves

Table 261. Solubilities of Synthetic Rubbers

Key

Rate of Action
- S—Slow
- M—Moderate
- F—Fast

Type of Action
- L—Limited Swelling and or softening
- G—Gelling or unlimited swelling
- D—Dissolving
- N—No apparent effect

SOLVENT	Boiling point °C. 760 mm.	Natural pale crepe	German Buna-S	GR-S	Hycar OS-10	Butadiene-methylmethacrylate copolymer	GR-I (butyl)	GR-M (Neoprene)	Perbunan 26	Hycar OR-15	GR-P ("Thiokol")	Plasticized polyvinyl chloride
I. Hydrocarbons												
A. Aliphatic												
Hexane	69	FD	FD	FD	MG	MD	FD	ML	SL	N	N	N
Hi-Test gasoline	38–141	FD	FD	FD	FL	FD	FD	ML	SL	N	N	N
Kerosene	165–257	FD	SD	SD	FL	FD	SD	SL	N	N	N	N
Mineral oil-aniline pt. 104° C.	—	FG	MG	MG	ML	MG	MG	SL	ML	N	N	N
B. Alicyclic												
Cyclohexane	80·8	FD	FD	FD	MD	FD	FD	MD	SL	N	N	N
C. Terpene												
Pinene	156	MD	MD	MD	FG	FD	MD	MD	FL	FL	N	SL
Dipentene	175–190	FD	FD	FD	MD	FD	FD	FD	FL	N	ML	SL
Turpentine	160–180	FD	FD	FD	MD	FD	FD	FD	FL	N	ML	SL
D. Aromatic												
Benzene	80·4	FD	FD	FD	FD	FD	FD	FD	FD	FL	FD	N
Toluene	111	FD	FD	FD	MD	FD	FD	FD	FD	FL	FL	N
Xylene	138–142	FD	FD	FD	FD	FD	FD	FD	FD	FL	FL	N
p-Cymene	175–176	FD	FD	MD	MD	FD	MD	FD	MD	FL	ML	N
Ethyl benzene	135·7	FD	FD	MD	MD	FD	MD	FD	FD	FL	FL	N
Styrene	145–146	FD	FD	FD	FD	FD	FD	FD	FD	FD	FD	FL
Tetrahydronaphthalene (Tetralin)	205	FD	FD	SD	SD	FD	MD	FD	MD	MG	FD	N
Amyl naphthalene	279–310	MD	SD	SD	SD	MD	MD	FD	MG	SG	FL	N
II. Halogenated Hydrocarbons												
A. Aliphatic												
Chloroform	61·2	FD	FD	FD	FD	FD	MD	FD	FD	FD	FD	ML
Carbon tetrachloride	76·7	FD	FD	FD	FD	FD	FD	FD	FL	N	N	N
Ethylene dichloride	83·5	FD	FD	FD	FD	FD	FG	FD	FD	FD	FD	SD
Isopropyl chloride	35	FD	FD	FD	FD	FD	FD	FD	FD	FG	ML	FL
Dichloro difluoro methane (Freon 12)	−28	FG	SL	SL	SL	SL	SG	N	N	N	N	N
Dichloro fluoro methane (Freon 21)	8·9	FD	SD	SD	MD	SD	MD	FG	FD	MD	MD	FL

B. Aromatic												
Chlorobenzene	132	FD	FD	FD	FD	FD	MD	FD	FD	SD	MD	ML
Fluorobenzene	84	FD	FD	FD	FD	FD	MD	FD	FD	FD	MD	FL
Chlorotoluene	159–162	FD	FD	FD	MD	FD	MD	FD	FD	FD	SD	ML
Ethyl pentachlorobenzene	—	SD	MD	MD	MD	MD	SD	MD	FL	ML	N	N
o-Chloronaphthalene	263	MD	FG	FG	FG	MD	MG	FD	MD	MD	MD	N
Halowax oil	—	MD	MD	MD	SD	MD	MG	MD	MD	MD	N	N
Amyl chloronaphthalene	—	SD	FG	FG	SG	MD	MG	MD	FG	N	ML	N
III. Hydroxy Compounds												
A. Alcohols												
Ethyl alcohol	78 3	N	N	SL	N	N	N	N	N	N	N	N
Isopropyl alcohol	82 4	ML	FL	FL	ML	ML	N	ML	FL	ML	ML	N
Amyl alcohol	137·8	N	N	N	N	N	N	N	ML	N	N	N
Benzyl alcohol	204·7	N	N	ML	ML	FL	N	FL	MD	MD	FD	N
Ethylene glycol	197·2	N	N	N	N	N	N	N	N	N	N	N
Diethylene glycol	244 8	N	N	N	N	N	N	N	N	N	N	N
Glycerin	290	N	N	N	N	N	N	N	N	N	N	ML
Terpineol	218–221	MG	MG	MG	ML	FG	SL	N	FL	N	N	N
B. Phenols												
Phenol	183	FL	N	SD	MD	MD	N	FL	MD	MG	FD	N
Cresol	190–203	N	N	FL	MG	MD	N	SG	MD	SD	MD	N
p-Tertiary butyl catechol	285	FL	N	N	FG	MD	N	N	FG	MG	FG	N
IV. Carboxy Acids												
Glacial acetic acid	118 1	N	N	FL	FL	N	FL	N	N	N	N	N
Lactic acid	119 (12 mm)	N	N	N	N	N	N	N	N	N	N	N
V. Ethers												
Diethyl ether	34 5	FD	FD	MD	MD	FD	FG	FL	N	N	N	N
Isopropyl ether	68·4	FD	FD	FD	SD	FD	FG	FL	N	N	N	N
Phenyl ethyl ether	172	MD	MD	MD	SD	FD	MG	SD	FD	SD	FL	N
Dibenzyl ether	295–298	MD	MD	MD	MD	FD	N	MD	MD	MD	SD	SL
Dioxane	101·1	SD	SD	SD	MD	FD	N	FD	MD	MD	FD	FL
Dioxolane	74	FL	SD	FD	FL	FD	FL	SD	MD	MD	MD	FL
VI. Amines												
Ethylene diamine	117·2	N	N	FL	ML	N	N	N	N	N	SD	N
Dicyclohexylamine	115–116 (8 mm.)	FG	FG	FL	SD	SD	FG	FG	FL	N	ML	N
Diethylamine	55–56	N	N	N	N	N	N	N	FG	N	N	N
Aniline	184·4	N	N	SL	MG	FL	ML	FL	MD	MD	MD	N
Dimethylaniline	194	FD	FD	FD	FD	FD	MG	FD	FD	FD	FD	MD
Phenylhydrazine	243·5	N	N	FL	MG	FG	ML	FG	FG	MG	FD	N

TABLE 261 (*continued*). SOLUBILITIES OF SYNTHETIC RUBBERS

KEY
Rate of Action
S—Slow
M—Moderate
F—Fast

Type of Action
L—Limited Swelling and or softening
G—Gelling or unlimited swelling
D—Dissolving
N—No apparent effect

SOLVENT	Boiling point C. 760 mm.	Natural pale crepe	German Buna-S	GR-S	Hycar OS-10	Butadiene-methylmethacrylate copolymer	GR-I (butyl)	GR-M (neoprene)	Perbunan 26	Hycar OR-15	GR-P ("Thiokol")	Plasticized polyvinyl chloride
VII. NITRO COMPOUNDS												
A. Aliphatic												
Nitromethane	101·2	N	N	N	FL	SD	N	FL	FD	FD	N	N
Nitroethane	114·0	N	SL	SL	FL	FD	N	FL	FD	MD	N	ML
1-Nitropropane	131·6	SL	SL	FL	FL	MD	N	FL	MD	MD	N	FL
1-Chloro-1-nitro ethane	122–128	MD	FD	FD	FD	FD	MD	FD	FD	FD	SD	ML
B. Aromatic												
Nitrobenzene	210	MG	SD	MG	MD	FD	N	FD	MD	MD	MD	MD
VIII. ALDEHYDES												
Furfural	161	N	N	N	N	N	N	N	FD	FD	FL	N
Benzaldehyde	179·5	FL	SD	MD	MD	FD	N	FD	FD	FD	FD	FL
n-Hexaldehyde	128·6	MG	MG	MG	MG	SD	N	N	FD	FD	N	N
IX. KETONES												
Acetone	56·1	N	N	N	SL	FL	N	FL	FD	FD	N	FL
Methyl ethyl ketone	80·6	FL	ML	MG	SD	FD	SL	FD	FD	FD	N	SD
Di-isopropyl ketone	123·7	FL	ML	MG	SD	FD	SL	FD	FD	FD	N	SD
Acetophenone	202	FL	FG	SD	SD	FD	N	FD	FD	MD	FD	SD′
Cyclohexanone	155–157	SD	SD	MD	SD	FD	SL	FD	FD	MD	FD	SD
Phorone	197·9	SD	SD	SD	FG	FD	N	MD	MD	MD	FG	FL
Mesityl oxide	128	FD	FD	FD	FL	FD	FL	FD	FD	MD	N	SD
X. ESTERS												
Methyl formate	32·3	FL	FL	FL	FL	FG	SL	N	SD	SD	ML	N
Ethyl acetate	77·1	FL	N	FL	FL	FG	ML	MD	MD	MD	N	ML
Butyl acetate	126·3	FD	FD	FD	MD	FD	ML	FD	MD	MD	N	ML
Butyl stearate	220–225 (25 mm.)	MD	SD	SD	FL	MD	MG	MD	N	N	N	N
Isopropyl acetate	88·4	FL	FG	FG	SD	FD	N	FD	FD	SD	N	FL
Ethyl oxalate	186·1	N	N	N	SL	N	N	FL	FG	MD	N	N

Amyl borate	143–147 (10 mm.)	FD	SD	SD	MG	N	FG	N	N	N	N	N
Benzyl benzoate	323–324	FL	SD	SD	MG	FG	N	MD	FG	MD	MD	N
Ethyl silicate	168·1	SL	ML	N	N	ML	N	N	N	N	ML	N
Ethyl acetoacetate	180·7	N	N	N	N	N	N	ML	MD	FD	N	N
Triacetin	258–259	N	N	N	N	N	N	N	N	N	N	N
Dibutyl phthalate	339·2	SL	MG	MG	MG	FG	N	MD	MG	SD	N	FL
Dioctyl phthalate	216 (5 mm.)	MG	MG	MG	SD	SD	N	SD	SG	N	N	FL
Tricresyl phosphate	295 (13 mm.)	N	ML	ML	ML	FL	N	ML	MG	MG	N	FL
Tributoxy ethyl phosphate	—	SL	SL	ML	ML	FL	ML	FL	FG	MD	N	ML
Butyl acetyl ricinoleate	220-235 (4 mm.)	FL	MD	MD	MD	FL	N	MD	MD	N	MD	FL
Methyl methacrylate	—	FD	FD	FD	SD	FD	ML	FD	FD	MD	SL	FL
Cottonseed oil	—	MG	MG	MG	MG	MG	N	N	SL	N	N	N
XI. Mixed Compounds												
A. Hydroxy Amines												
Triethanolamine	208 (10 mm.)	N	N	ML	ML	N	N	ML	N	N	ML	N
B. Alcohol Ethers												
" Cellosolve "	135·1	FL	FL	N	N	FG	N	N	FL	N	N	N
Butyl " Cellosolve "	171·2	N	N	N	N	FL	N	ML	N	N	N	N
" Cellosolve " acetate	156·3	ML	ML	FL	ML	FL	N	MD	MD	MD	N	N
" Carbitol "	201·9	FL	N	ML	ML	FL	N	N	N	N	N	N
C. Chlorinated Alcohols												
Ethylene chlorohydrin	128·7	FL	N	ML	ML	N	N	N	MD	MD	FL	N
XII. Heterocyclics												
Piperidine	106	FD	FD	MD	SD	FG	MD	FD	FG	MG	FD	SD
Furan	31·5	FD	FD	FD	FG	FD	FL	FD	FD	FG	N	N
Thiophene	84	FD	FD	FD	FD	FD	FL	FD	FD	FD	FD	FL
Pyridine	115	FG	FD	MD	FD	FD	N	FD	FD	FD	MD	SD
Pyrrole	130	FL	N	N	N	N	N	FD	FD	FD	FD	N
XIII. Sulphur Compounds												
Carbon disulphide	46·2	FD	FD	FD	FD	FD	MD	FD	SD	ML	FG	N
Ethyl mercaptan	36–37	FD	FD	FD	FG	FD	FD	FD	FD	FG	FG	N
Liquid sulphur dioxide	— 10	ML	ML	ML	ML	ML	N	SL	MD	FD	FD	ML
XIV. Miscellaneous												
Acrylonitrile	78–79	N	N	MD	MD	FL	FL	SL	MD	FD	N	N
Formamide	193d	N	N	N	N	N	N	N	N	N	N	N
" Dispersing Oil 10 "	225–300	FD	MD	MD	MD	FD	FL	MD	MD	MD	MG	FL
" Bardol B "	230–300	FD	MD	MD	MD	FD	MG	FD	MD	MD	MG	FL
" Nevoll "	—	MG	MG	FG	SD	FG	N	FL	FL	FL	N	FL
Liquid ammonia	— 33·4	SL	SL	SL	SL	SL	SL	N	N	ML	FG	ML
" Circo Light Processing Oil "	—	SD	FL	FL	ML	FL	FL	FL	N	N	N	N

a gum will produce pronounced swelling action on the corresponding vulcanizate.

In applying these data to vulcanized compounds, allowances must be made for the degree of vulcanization, pigment loading, and the presence of plasticizers or softeners which may or may not be extracted by the solvent under consideration.

Thus by proper interpretation of these studies it is possible to find the answers to many practical questions which arise daily in rubber technology. Sarbach and Garvey gave the following few examples to illustrate practical use of the table :

1. Q. Which solvents could be expected to serve best for the manufacture of " Thiokol " solvents ?
   A. Dioxane, acetophenone, cyclohexanone, benzene, styrene, chloroform, ethylene dichloride, and benzyl alcohol all show excellent solvent action on " Thiokol ".
2. Q. Which chemical group of solvents would be most practical for dissolving a vinyl resin such as is contained in Koroseal products and an acrylonitrile butadiene synthetic such as Hycar OR or Perbunan or a blend of the two materials ?
   A. The ketones appear to be the most logical choice.
3. Q. Which general classification of plasticizers would be expected to have the greatest softening action on Hycar OR or Perbunan ?
   A. From the action of the solvents, high boiling, high molecular weight esters, ketones, chlorinated hydrocarbons, and compounds containing the benzyl group should be most effective.
4. Q. Which general classification of plasticizers would be expected to have the greatest softening action on GR-S ?
   A. The solvent data indicate that the hydrocarbons in general should be most effective.
5. Q. Which of these elastomers would serve best for making a hose tube to deliver aniline ?
   A. Interpretation of the data shows that natural rubber would serve best for this application.
6. Q. If a storage tank were to be lined with a rubbery composition to resist the action of pyridine or dioxane, which of these elastomers would serve best or be least affected by the solvents ?
   A. The solvent data show that butyl rubber would be expected to be least affected by either solvent.
7. Q. Which of these elastomers would serve best for compounding a gasket used to seal against carbon disulphide ?
   A. Hycar OR-15 and Koroseal products are apparently affected least by this solvent.

The brittle point or crack point at low temperatures is one of the most important characteristics of materials. A comprehensive investigation on this point has been carried out by Selker, Winspear and Kemp.[15]

TABLE 262. CHEMICAL RESISTANCE AT 20° C.

	Rubber	Buna-S	Perbunan	Hycar	Chemigum	Neoprene	Thiokol A	Poly-isobutylene	Butyl rubber	Polyvinyl chloride+ tricresyl phosphate	Highly polymerized acrylic acid esters
H_2O	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Fairly good
O_2 + Light	Poor	Moderate	Good	Good	Good	Good	Good	Fairly good	Moderate	Good	Good
Ozone	Poor	Moderate	Fairly good	Fairly good	Fairly good	Fairly good	Good	Good	Good	Good	Good
H_2SO_4 conc.	Poor	Poor	Moderate	Moderate	Moderate	Good	Good	Good	Good	Moderate	Moderate
H_2SO_4 dilute	Moderate	Moderate	Good	Good	Good	Good	Good	Good	Good	Good	Moderate
HNO_3 conc.	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Fairly good	Good	Moderate	Moderate
HNO_3 dilute	Good	Poor	Moderate	Moderate	Moderate	Moderate	Poor	Good	Good	Moderate	Moderate
HCl conc.	Moderate	Moderate	Fairly good	Fairly good	Fairly good	Good	Poor	Good	Good	Moderate	Moderate
HCl dilute	Good	Good	Good	Good	Good	Good	Fairly good	Good	Good	Good	Moderate
Acetic acid con.	Moderate	Moderate	Good	Good	Good	Good	Good	Good	Good	Moderate	Poor
,, ,, 10%	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Fairly good
KOH conc.	Moderate	Moderate	Good	Good	Good	Moderate	Poor	Good	Good	Fairly good	Poor
KOH dilute	Good	Good	Good	Good	Good	Moderate	Moderate	Good	Good	Good	Moderate
Alcohols	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Moderate
Esters	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Good	Good	Good	Poor	Poor
Ether	Poor	Poor	Good	Good	Good	Good	Good	Moderate	Good	Fairly good	Poor
Acetone	Good	Good	Moderate	Moderate	Moderate	Good	Good	Good	Good	Poor	Poor
Petrol	Poor	Poor	Good	Good	Good	Good	Good	Poor	Poor	Good	Good
Benzene	Poor	Poor	Poor	Poor	Poor	Poor	Good	Poor	Poor	Poor	Poor
Transformer oil	Poor	Poor	Good	Good	Good	Good	Good	Poor	Poor	Good	Good

TABLE 263. BRITTLE POINT OF SYNTHETIC ELASTICS

Compound	Cure		Brittle point ° C. (±0·5°)
	Temp. ° C.	Time min.	
Polychloroprene—			
Milled 5 min.	109	10	−36·8
Gum stock	142	30	−38·5
+3 parts soft black +8 parts oil	142	20	−40·6
Gum stock + 5 parts channel black + 20 parts oil	142	30	−42·5
Gum stock + 100 parts soft black + 8 parts oil	142	30	−36·4
Gum stock + 200 parts soft black + 10 parts oil	142	30	−32·0
Butadiene polymer—			
Milled 5 minutes	135	10	−67·8
Gum stock	148	60	65·5
Tyre tread stock	148	60	−71 to −69
Butadiene-styrene copolymer—			
Milled 2 minutes	153	30	65·5
Gum stock	148	60	65·5
Tyre tread stock	148	60	−66 to −70
Butadiene-acrylonitrile copolymer—			
American	—	—	−49 to −52
German	148	15	−45·5
Gum stock	142	45	−42 to −45
Tyre tread stock	142	45	46·5
Butadiene-nitrile copolymer, type—			
Milled 5 minutes	148	10	−25·6
Gum stock	153	45	−24·5
Clay loaded stock	153	45	−29·0
Soft stock (d.b.p. 50 parts)	153	45	−42·5
Butadiene-nitrile copolymer, Type II—			
Milled 1 minute	—	—	−29·3
Gum stock	153	45	−29·5
Tyre tread stock	153	30	−26 to −28
Organic polysulphide—			
Type 1	—	—	+ 7·0
Type 1 carbon black stock	142	50	− 3·8
Type 2 carbon black stock	148	30	−22·5
Type 3	—	—	−35·3
Type 3 carbon black stock	148	50	−34·0
Type 4	—	—	−35·5
Type 4 carbon black stock	142	50	39·5

McCrary [10] and collaborators have prepared some useful comparative data on wire insulation. The electrical characteristics of 40 per cent. wire insulation, using different synthetic rubbers, are shown in the following table:

TABLE 264. ELECTRICAL PROPERTIES OF COMPARABLE ELASTIC MIXES

Type	Dielectric strength (volts per mil.)		Dielectric constant	
	Dry	96% Humidity	Dry	96% Humidity
Natural rubber	498	482	3·35	4·24
25% Vistanex M	442	434	3·53	5·65
50% Vistanex M	442	429	3·51	4·66
Neoprene GN	360	356	7·33	7·74
Neoprene I	330	340	10·2	12·2
Hycar OR	396	241	14·7	20·2
Chemigum I	373	170	11·9	15·1
German Perbunan	342	157	11·6	17·0
Domestic Perbunan	379	243	11·0	14·8
Thiokol RD	403	120	12·0	22·6
Thiokol F	300	132	11·1	48·6
Thiokol FA	287	180	9·05	32·4

Type	Power factor		Insulation resistance (megohms at 180 volts)	
	Dry	96% Humidity	Dry	96% Humidity
Natural rubber	0·0031	0·0446	2,000,000+	820,000
25% Vistanex M	0·0016	0·0565	2,000,000+	2,000,000
50% Vistanex M	0·0019	0·0728	2,000,000+	670,000
Neoprene GN	0·0177	0·0204	1,550	1,100
Neoprene I	0·0368	0·0418	880	400
Hycar OR	0·0233	0·137	200	10·4
Chemigum I	0·0729	0·227	140	7·1
German Perbunan	0·0454	0·155	86	10·5
Domestic Perbunan	0·0527	0·160	85	11·0
Thiokol RD	0·0723	0·130	158	26·5
Thiokol F	0·0081	0·316	580	10·5
Thiokol FA	0·0041	0·234	6,400	80

Gas Permeability of Fabrics coated with Synthetic Rubbers. The gas permeability of coated fabrics have been described by the U.S. Bureau of Standards. Some of the results observed in these tests are as follows: (1) The permeabilities of most types of synthetic rubbers are lower than that of natural rubber. (2) The rate of gas permeation of neoprene is about one-fourth that of natural rubber. (3) The rate of permeation of GR-S is nearly the same as that of natural rubber.

(4) The permeability of rubber to helium is about two-thirds of its permeability to hydrogen. (5) Carbon dioxide penetrates rubber at a rate 2·9 times that of hydrogen. (6) Rubbers of the butadiene-acrylic nitrile type have about the same rates for the three gases. (7) In the case of butyl rubber and polyisobutylene, the permeability of helium is slightly greater than hydrogen and the rate of passage of carbon dioxide is slightly more than one-third that of hydrogen.

TABLE 265. COMPARATIVE PROPERTIES OF SPONGE RUBBERS
(Proper compounding for desired properties is assumed)

Base material	General characteristics	Heat resistance	Low-temperature compressibility	Swelling in petroleum base oils	Flame resistance	Compression set
Natural rubber	Good	Good	Good	High	Burns	Excellent
Buna-S (GR-S)	Good	Good	Good	High	Burns	Good
Buna-N	Good	Good	Poor	Low	Burns	Good
Neoprene-GN (GR-M)	Good	Good	Poor	Medium	Does not burn	Good
Neoprene-FR	Good	Good	Good	Medium	Burns	Excellent
Butyl (GR-I)	Good	Fair	Fair	High	Burns	Fair
Plasticized vinyl chlorides	Good	Poor	Poor	Medium	Does not burn	Fair

REFERENCES

[1] BARNES, WILLIAMS, DAVIS and GIESECKE, *Rubber Chem. Tech.*, 1944, **16**, 254.
[2] BUNN, *Trans. Faraday Soc.*, 1939, **35**, 483.
[3] BURCHFIELD, *Ind. Eng. Chem.* (Anal), 1945, **17**, 806.
[4] CAROTHERS, *Ind. Eng. Chem.*, 1934, **26**, 30.
[5] FULLER, *Chem. Rev.*, 1940, **26**, 143.
[6] FULLER, FROSCH and PAPE, *I.R.W.*, 1940, **102**, 61.
[7] HALLE and HOFFMAN, *Naturwiss.*, 1935, **23**, 770.
[8] KLUCKOW, *Chem. Zeitung.*, 1941, **45**, 63.
[9] LOTMAR and MEYER, *Monatsh.*, 1936, **69**, 115.
[10] MCCRARY and Collaborators, *India Rubber World*, 1942, **107**, 271.
[11] MALDWYN JONES, *Proc Rubber Tech. Conf.*, 1938, p 411.
[12] Ministry of Supply—Users Memorandum No. U.9.
[13] Physical Properties, *Chem. Met. Eng.*, 1942, **49**, 97.
[14] SARBACH and GARVEY, *India Rubber World*, 1947, **115**, 798.
[15] SELKER, WINSPEAR and KEMP, *Ind. Eng. Chem.*, 1942, **34**, 160.
[16] WHITBY and KATZ, *Ind. Eng. Chem.*, 1933, **25**, 1204.
[17] WOOD, *Ind. Eng. Chem.*, 1942, **34**, 1293.
[18] WOOD, U.S. Dept. of Commerce, Circular C. 427, 1940

NAME INDEX

SUBJECT INDEX